THE CONDENSATION Of ACETONE And SIMILARLY REACTIVE METHYLENE COMPOUNDS With ANTHANTHRONE And RELATED COMPOUNDS.

By

ALISTAIR GREGOR MacGREGOR, B.Sc.

Thesis for the Degree of Doctor of Philosophy.

June 1941.

University of Edinburgh.

I N D E X.

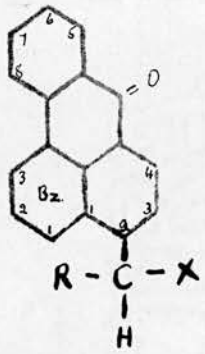
I N T R O D U C T I O N.

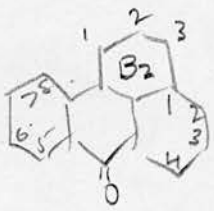
The condensation of acetone and similarly reactive methylene compounds with benzanthrone in the presence of alkaline condensing agents has been described in B.P. No. 319,593. According to this process, valuable new derivatives of the benzanthrone series are obtained when benzanthrone, or a substituted benzanthrone with free 2-position, is condensed with a compound of the general formula $X\text{-}CH_2\text{-}R$ in the presence of an alkaline agent such as solid potassium hydroxide. In this formula, X represents a nitrile group NC-, an acid amido group $NH_2\text{-}CO\text{-}$, or an acyl group R'-CO- . In the latter case the reacting compounds are ketones of the formula $R'\text{-}CO\text{-}CH_2\text{-}R$ in which R' is a hydrocarbon radical which may contain other substituents. In both instances R represents a hydrogen atom, an alkyl or aryl group which may be substituted, or an esterified carboxylic group.

Considerable latitude in the conditions under which the reactions take place is indicated in the original patent. Thus the condensation may be effected in organic diluents such as benzene, mono-, di-, or tri-chlorobenzene, pyridine, and the like, and in an excess of the organic compound to be condensed. The reaction may be carried out while excluding air -

for instance, in a nitrogen atmosphere, or in the presence of air if desired. It is claimed that the condensations take place readily and that good yields are obtained.

The products formed in these condensations are considered to correspond to the following formula in which -R and -X represent the group or groups already indicated:-



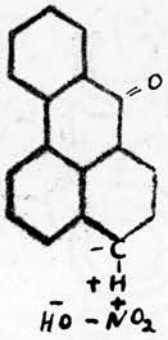


The above system of numbering the benzanthrone molecule is that used by the Journal of the Chemical Society and will be employed throughout this thesis.

Under ordinary circumstances the 2-position is not the most reactive in the benzanthrone molecule. During nitration (in nitrobenzene solution), or chlorination, for example, the Bz. 1-position is first attacked. Introduction of a second chloro-group is usually effected in the 6-position. Oxidation of benzanthrone by means of manganese dioxide and concentrated sulphuric acid at 0°C. results in the Bz. 2-position being attacked with the production of Bz. 2-hydroxy-benzanthrone.

When benzanthrone is nitrated in nitrobenzene

solution by means of concentrated nitric acid, the primary product is Bz. 1-nitro-benzanthrone.



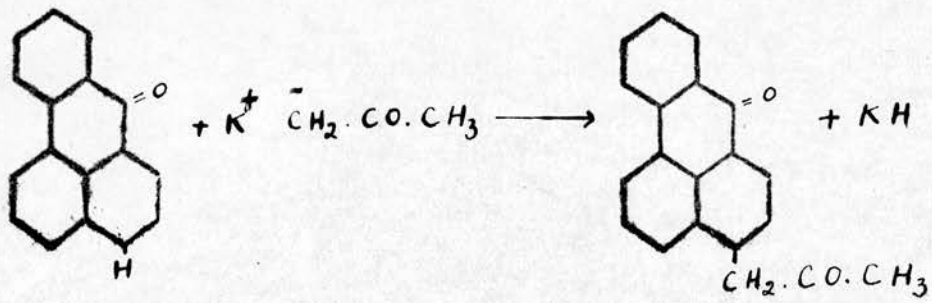
The nitric acid may be represented as the polar form $\overset{-}{HO}\text{-}\overset{+}{NO_2}$. The positive $-NO_2$ group then attacks the Bz. 1-position in the benzanthrone molecule which is thus assumed to be a negative centre. When acetone is condensed with benzanthrone in the presence of powdered potassium hydroxide, the 2-position is attacked. In this instance it might be assumed that the complex

$$\overset{+}{K} \mid \overset{-}{CH_2}.CO.CH_3$$

is formed with the potassium hydroxide and acetone, or a resonance hybrid of this form with the form

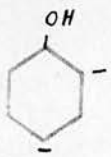
$$\overset{+}{K} \mid CH_2=\overset{\overset{-}{O}}{\overset{|}{C}}-CH_3 \ .$$

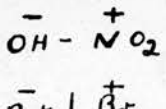
The 2-position in the benzanthrone molecule must then be represented as a positive centre. The condensation would then take place in the following way:



Known examples illustrate the above reasoning. For instance, phenol on bromination or nitration yields ortho- and para-derivatives; therefore positions 2 and 4 are negative centres:

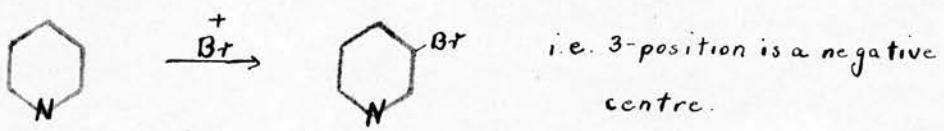
i.e.,



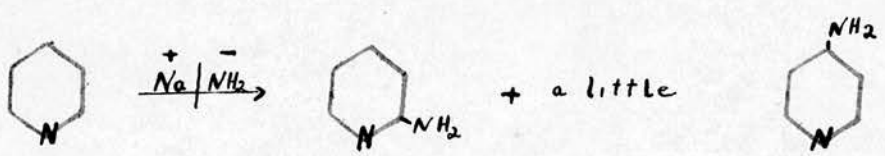


Thus nitric acid and bromine are called <u>Cationoid Reagents.</u> In the case of nitrobenzene which has positive centres at positions 2 and 4, these substituents go to the meta-position. m-Dinitrobenzene reacts with potassium cyanide as follows:-

Here also it is assumed that the 2-position is a positive centre. Again in the case of pyridine:-

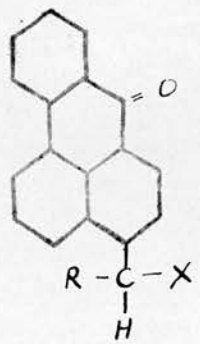


<u>but</u>



This last reaction is a closer analogy with the acetone condensation under consideration.

The products represented by the formula



can be converted by the action of alkaline agents into salt-like compounds, for example, in the presence of alcohol or acetone. During this process the group R-CH-X usually forms a characteristically and strongly coloured solution in the alcoholic medium. Dilution of these solutions with water generally effects hydrolysis of these salt-like compounds.

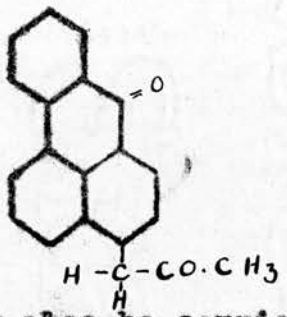
The preparation of several of these condensed benzanthrone products is fully described in the patent and the condensation of benzanthrone with acetone in the presence of powdered caustic potash may be usefully cited as a typical example.

Preparation of 2-acetonyl-benzanthrone.

200 parts of acetone are dropped, while stirring, into a mixture of 100 parts of benzanthrone, 400 parts of powdered caustic potash, and 3000 parts of benzene, at a temperature of about 20°C., the stirring being continued for three hours at the same temperature. The parts are by weight. The colour of the mixture changes from brownish-yellow to greenish-yellow and finally to blue-green or olive-green. The mixture,

while being cooled, is then diluted and simultaneously acidified with dilute hydrochloric acid, and the benzene layer is freed from water and concentrated until crystallisation takes place.

The resulting ketone crystallises in compact, golden-yellow crystals, melting at from 189 to 190°C. It dissolves to an intensely blue solution, with reddish tinge, in alcoholic solutions of alkali metal hydroxides and the like, and to an orange solution, with yellow-brown fluorescence, in concentrated sulphuric acid. The formula assigned to this product is that of 2-acetonyl-benzanthrone, viz :



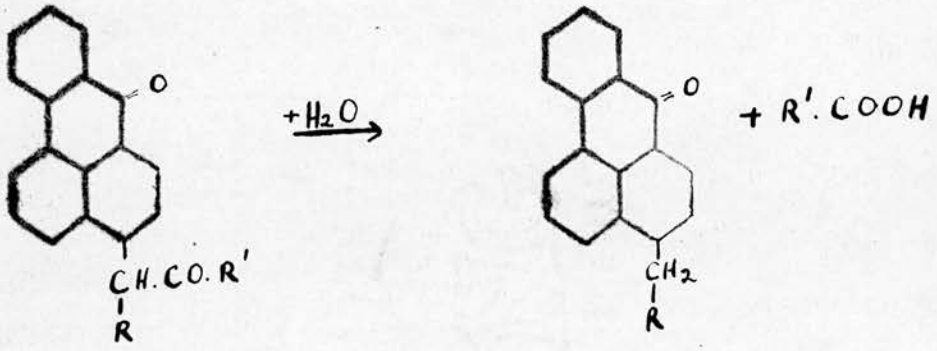
The condensation may also be carried out with other alkaline condensing agents such as caustic soda or sodium alcoholates and may be conducted with the exclusion of air, for example, in a nitrogen atmosphere.

Among other condensations quoted are those between benzanthrone and higher reactive ketones under the conditions described above, and the condensation of benzanthrone with reactive amides and nitriles in an atmosphere of nitrogen, using pyridine as diluent. Various modifications in the conditions under which the

reactions take place are indicated in several instances. For example, the time of contact of the reagents and the temperature at which the reaction is carried out vary in the examples quoted but no precise information is offered as to the influence of such factors on the course of the condensation.

The hydrolysis of several of these benzanthrone derivatives is described in a later patent, B.P. No. 322,253. The cleavage of the condensation products with alkaline hydrolysing agents such as caustic alkalis or weak alkaline agents, for example, calcium hydroxide, barium hydroxide, takes place very readily, and good yields of, for example, 2-methyl-benzanthrone and acetic acid are obtained by heating 2-acetonyl-benzanthrone in 5% alcoholic potash solution. In many cases it is preferable to carry out the preparation of the condensation products and the splitting up of the same in one operation. By this means 2-methyl-benzanthrone has been prepared from 2-phenacyl-benzanthrone and 2-n-propyl-benzanthrone from the condensation product of di-n-propyl-ketone with benzanthrone, the secondary products of the hydrolyses being benzoic and n-butyric acids respectively.

The general equation for the hydrolysis of the condensed product is represented below, the reaction taking place under the influence of aqueous or alcoholic caustic alkali:-



Thus it is claimed that the technically important 2-methyl-benzanthrone, which hitherto could only be obtained from 2-methyl-anthraquinone, becomes readily accessible, and that the process permits the preparation of hitherto unknown 2-substituted homologues of benzanthrone in which hydrogen in the 2-position is replaced by an alkyl group containing more than two carbon atoms. These compounds may be further substituted in the benzanthrone ring system. Products of this type may be used in the preparation of dyestuffs. No claim whatsoever is made in the patent concerning the hydrolysis of any condensed benzanthrone in which the side chain is other than that obtained from the condensation of benzanthrone with a ketone.

As an example of the preparation of a condensed benzanthrone derivative and of its hydrolysis in one operation, the following preparation may be described:-

Preparation of 2-methyl-benzanthrone.

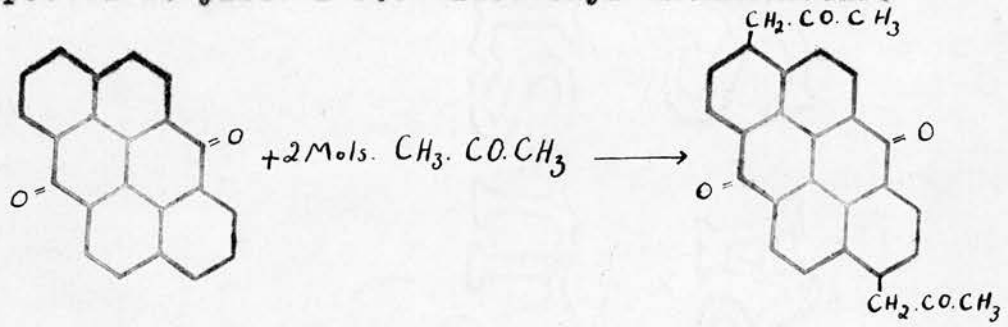
10 parts of acetone are introduced while stirring at room temperature in an atmosphere of nitrogen, into a mixture of 10 parts of benzanthrone, 20 parts of

powdered caustic potash, and 40 parts of monochlorobenzene, and the whole is stirred at the same temperature for about three hours. The reaction mixture is then diluted with 100 parts of alcohol and boiled under a reflux condenser for about three hours. The product which crystallises out after cooling is practically chemically pure 2-methyl-benzanthrone of a melting point of about 198-200° C.

The foregoing is substantially an outline of all the available information on these new processes for the preparation of condensation products of the benzanthrone series in the presence of alkaline condensing agents, and of their subsequent hydrolysis. Yields are not quoted nor is the significance of certain modifications in the conditions of condensation indicated. It is claimed, however, that the scope of the process is not limited to the examples listed. The reactions involved therefore lend themselves to the investigation of condensations of reactive methylene compounds with other cyclic compounds of similar type in the presence of alkaline condensing agents, and to a study of the influence of hydrolysing agents on the products. This is the subject of the present thesis.

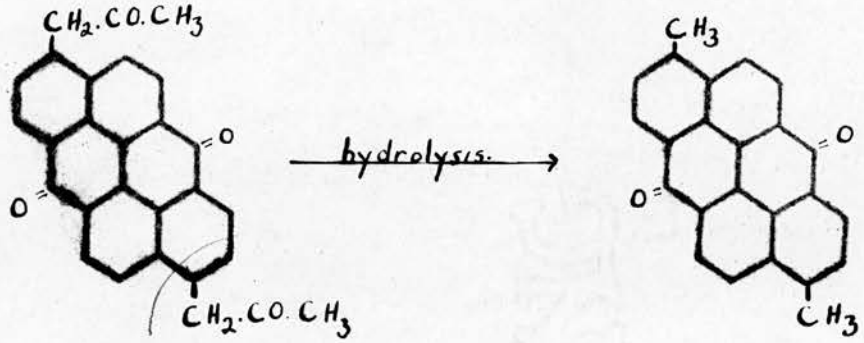
It was proposed, in the first instance, to attempt the condensation of acetone with anthanthrone in the presence of powdered caustic potash as condensing agent.

An indication that a reaction of some kind occurred with the above reagents was received from the I.C.I. laboratories at Blackley but no further information was available. By analogy with benzanthrone, where the reactive position is para to the ketonic group, the anthanthrone molecule should have two reactive positions at 3:8 and the condensation, if successful, would be expected to yield a 3:8-diacetonyl-anthanthrone.



Anthanthrone. 3: 8 - Diacetonyl-anthanthrone.

This latter compound would be interesting if it reacted under the influence of alkaline hydrolysing agents in a manner analogous to that of 2-acetonyl-benzanthrone. Under the influence of alkaline hydrolysing agents 2-acetonyl-benzanthrone splits off acetic acid and yields the commercially important 2-methyl-benzanthrone. Under the same conditions 3:8-diacetonyl-anthanthrone might be expected to yield two molecules of acetic acid and 3:8-dimethyl-anthanthrone. This latter derivative would be a dyestuff and is of technical interest.



3:8-dimethyl-anthanthrone.

The condensation, therefore, if successful in the case of acetone and anthanthrone, should open up a wide field of possibilities in the extension of the process to other reactive methylene compounds such as acetophenone, acetonitrile, and phenylacetonitrile. The diacetophenone derivative of anthanthrone would presumably hydrolyse, yielding two molecules of benzoic acid and one molecule of dimethyl-anthanthrone, but the behaviour towards hydrolysing agents of the acetonitrile and phenylacetonitrile derivatives of anthanthrone is an unknown factor. No indication as to the behaviour of the corresponding benzanthrone derivatives is vouchsafed in the patent, and it is conceivable that choice of reagent might result in various cleavages of the side chain.

The present work was undertaken on the suggestion of Imperial Chemical Industries Limited., Dyestuffs Group, in order to determine whether the method could be adapted for the preparation of dimethyl- and especially of monomethyl-anthanthrones. If time

permitted it was also intended to examine the possibility of extending the reaction to other complex cyclic ketones and similar compounds, such as helianthrone, 1:9-pyrazole-anthone, N-methyl-1:9-anthrapyramidine, and 1:9-anthrapyridine.

It will be noted that the above represents a very wide field on which no information is available in the literature. In most of these cases the compounds are highly insoluble and infusible and it will not be possible to check the purity of prepared derivatives by melting point, or the identity of two fractions by mixed melting point. Information on these points will therefore have to be gained from analytical data, comparative solubility tests, colour reactions, etc., and progress will necessarily be considerably slower than if the normal melting point tests had been applicable. For this reason it was decided to make a rapid survey of a number of the compounds in question, in their reaction towards powdered potassium hydroxide and acetone, and then to make a more detailed investigation of anthanthrone if it gave indications of reacting in the desired direction.

Simultaneously with the foregoing scheme of work it was proposed to make a study of the influence of hydrolysing agents on 2-benzylcyano-benzanthrone prepared by the process described in the patent. No mention of this treatment is made in the patent and a dual

purpose will be served by this investigation, namely, an attempt to gain information about the effect of hydrolytic agents on the benzylcyano-derivatives, and to gain an insight into the probable behaviour of the corresponding derivatives of anthanthrone if they should prove obtainable. XX

EXPERIMENTAL RESULTS And DISCUSSION.

CONDENSATION Of ACETONE With ANTHANTHRONE.

The results of many experiments carried out during the course of this work have shown that the condensation of acetone with anthanthrone in the presence of powdered potassium hydroxide undoubtedly occurs to some extent. This is evident from the fact that on merely shaking a mixture of anthanthrone, acetone, and powdered potassium hydroxide in a diluent such as pyridine, an intense green colouration develops within ten minutes at room temperature. This corresponds closely to the behaviour of the above mixture when benzanthrone is used in place of anthanthrone. In the latter case a blue-green colouration is produced which is due to the formation of an enolic salt of acetonyl-benzanthrone. Such salts furnish intensely coloured solutions in solvents such as alcohol or acetone, and the development of a green colouration in the case of the acetone-anthanthrone condensation leads to the conclusion that a similar reaction occurs in this case.

In the first instance, a condensation was attempted under the conditions prescribed in the patent

for the condensation of acetone with benzanthrone using a proportionate amount of anthanthrone. The acetone was dropped into a stirred mixture of anthanthrone, benzene, and powdered caustic potash, and stirring continued for three hours at room temperature. No colour change occurred in the interval but on acidifying the mixture, filtering, and separating the benzene layer, an olive green colouration developed on testing this solution with methyl alcoholic potassium hydroxide solution. The orange-red residue gave no such colour on testing in a similar manner, and dissolved to a green solution in concentrated sulphuric acid. From these latter tests and by comparison of the weight of recovered material with the weight of anthanthrone employed, it was evident that the bulk of the anthanthrone had been recovered unchanged. The reaction thus appeared to proceed to a very small extent and the presence of an enolic derivative in the benzene layer indicated that the progress of the reaction was in proportion to the small amount of anthanthrone dissolved in the benzene.

Anthanthrone is only very slightly soluble in benzene in the cold, whereas benzanthrone is quite soluble. Thus a search was made for a more suitable diluent. On testing the solubility of anthanthrone in various solvents, pyridine and nitrobenzene appeared to hold most anthanthrone in solution at room

temperature. Nitrobenzene was, however, considered unsuitable for a condensation involving the use of an alkaline agent because of the possibility of it being reacted upon. A condensation was therefore carried out using pyridine as diluent and increasing the proportions of all the reagents with respect to anthanthrone.

The condensation was carried out while maintaining the temperature at 20-25° C. In this instance, colour changes very similar to those occurring during the condensation of acetone with benzanthrone were in evidence. The original orange-red mixture turned chocolate-brown on addition of the acetone, and after ten minutes the mixture was an olive-green colour. A deep green persisted throughout four and one quarter hours of stirring. The mixture was then diluted with alcohol, simultaneously acidified and cooled, and allowed to stand overnight. On filtration, a dark brown solid (A) was obtained and the filtrate (B) was brown with greenish fluorescence. The solid was washed well with water, dried at 60-70°C., and was found to be of the same weight as that of anthanthrone reacted upon. On testing a small portion with methyl alcoholic potassium hydroxide solution, a clear green colour developed, whereas the filtrate (B) gave a blue colour with the same reagent.

Examination of the filtrate by extraction with

solvents showed that the colour was mainly due to resinous material with a trace of some enolic compound. The dark brown residue (A) was therefore examined with a view to the separation of the component forming a green potassium salt in methyl alcohol solution. Aqueous 2 N-sodium hydroxide extracted no alkali soluble material but shaking for twenty minutes with 0·5 normal methyl alcoholic potassium hydroxide solution and filtering produced a dense green filtrate and a brownish-black residue. On weakly acidifying this filtrate with dilute acetic acid, a small brown precipitate appeared which, on separation, represented a yield of about 1% of alkali soluble material.

This then appeared to be a practicable method for the separation of any enolic derivative formed in the condensation and it was decided to apply it in a new condensation. In order to force the condensation further in the desired direction the proportion of the reagents with respect to anthanthrone was again increased tenfold, 100 gms. acetone being dropped into a stirred mixture of 3 gms. anthanthrone, 200 gms. anhydrous pyridine, and 20 gms. powdered potassium hydroxide, and the stirring continued for six hours at 20-25°. The same series of colour changes occurred in this case and the washed and dried residue, which weighed 3·0 gms., was treated by shaking in the cold with 360 ml. of 0·5 N methyl alcoholic potassium

hydroxide solution as before. Since no information was available at this stage concerning the stability to alcoholic alkali of the supposed acetonyl derivative, the time of contact of the solid with the alcoholic alkaline solution was kept as short as possible. In this instance, 9% of alkali soluble material was separated.

This alkali soluble material gave the expected green colour with methyl alcoholic potassium hydroxide solution and also dissolved in concentrated sulphuric acid to a permanganate pink solution with golden fluorescence, thus showing a behaviour different to that of anthanthrone. However, the alkali insoluble residue gave similar colour reactions with these reagents, and it was evident that a complete extraction of the enolic content had not been effected. It was therefore decided to investigate the possibility of separating the components of this residue by means of organic solvents. Its solubility was tested in various solvents and monochlorobenzene appeared most suitable.

An extraction was first carried out by boiling the residue with chlorobenzene, cooling, and filtering. Most of the residue was left on the filter but the solution was strongly coloured reddish-brown. This solution was examined by the chromatographic method in a calcium carbonate adsorption tube. The adsorbent separated a bright orange band which contained nearly

all the solid in the chlorobenzene solution, and on recovering and testing the solid with concentrated sulphuric acid, it gave the characteristic colour reaction of anthanthrone. It also produced no colour with methyl alcoholic potassium hydroxide solution. On testing the residue (insoluble in cold chlorobenzene) with methyl alcoholic potassium hydroxide solution, a green colour again developed, indicating the presence of the enolic derivative. It therefore appears that the condensation product is less soluble in chlorobenzene than the parent anthanthrone, and that the introduction of acetonyl groups does not, as was expected, increase the solubility in organic solvents.

The residue insoluble in cold chlorobenzene was then added to the solid extracted previously by methyl alcoholic potassium hydroxide solution, the whole boiled with chlorobenzene and filtered hot. The filtrate, on cooling, deposited a brownish microcrystalline precipitate which was separated and freed from solvent. A portion of this precipitate gave a green colour on gently warming with methyl alcoholic potassium hydroxide solution and dissolved in concentrated sulphuric acid to a fluorescent permanganate coloured solution. Analysis of a sample of this product gave C = 78·7, H = 4·44%. The figures for a diacetonyl anthanthrone are C = 80·4, H = 4·3%. A mono-acetonyl d erivative would require C = 82·9, H = 3·87%,

while the corresponding figures for anthanthrone are C = 86·3, H = 3·27%. The above experimental analysis figures therefore suggest that an impure diacetonyl-anthanthrone had been isolated.

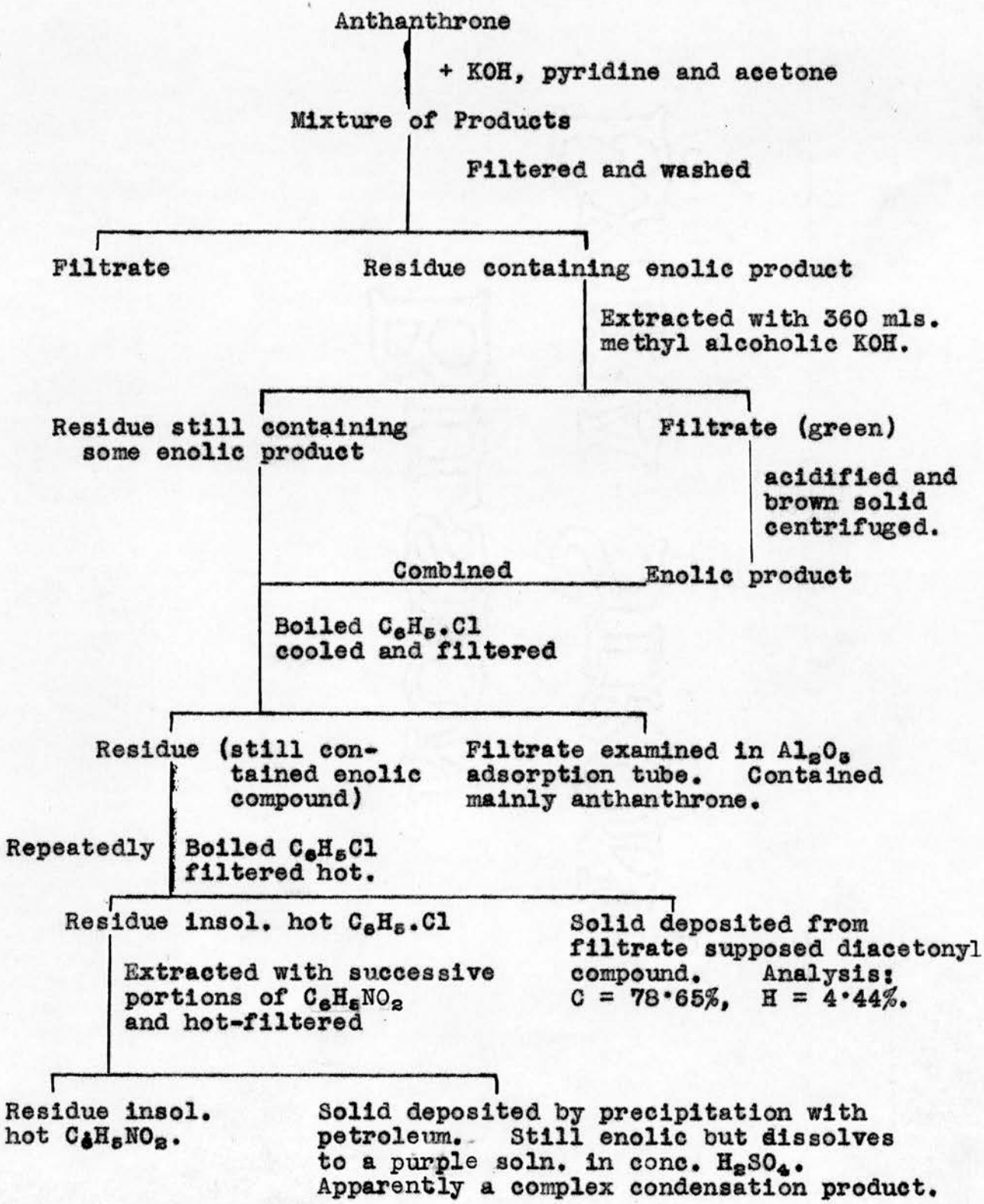
A sample of this anthanthrone derivative was boiled under reflux with a 5% methyl alcoholic solution of potassium hydroxide. A green colour developed immediately but after two hours the solution was brown with only a greenish tinge. Further boiling did not discharge this green tint. On acidification and recovery of the dark brown solid, a sample was tested with concentrated sulphuric acid and gave a brownish-green solution. On "vatting" the remainder, which weighed only a few milligrammes, cotton was dyed a light brown colour from a violet-red vat.

Meanwhile the residue from which this sample of the condensation product had been extracted was again repeatedly boiled with fractions of chlorobenzene, filtered hot, and precipitated with light petroleum until extraction was complete. In this way a further small quantity of acetonyl derivative was recovered. The combined weights of these fractions of acetonyl-anthanthrone amounted to about 8% yield.

The residue, insoluble in hot chlorobenzene, was then treated in a similar manner with nitrobenzene, and on recovery of the solid extracted and testing with concentrated sulphuric acid, a purple colour formed with no fluorescence. A faint green colour developed

with a sample of this solid on heating with methyl alcoholic potassium hydroxide solution. Further treatment of the residue with nitrobenzene extracted more of this solid but some material remained completely insoluble.

The above processes may be summarised as follows:-



Thus from this condensation of acetone with anthanthrone three main fractions differing in solubility in chlorobenzene appear to have been isolated. Firstly, some unchanged anthanthrone can be removed by extraction with cold chlorobenzene. From the residue, by extraction and precipitation from hot chlorobenzene, a compound which is possibly a diacetonyl derivative may be obtained, and lastly there remains a fraction completely insoluble in hot chlorobenzene. This latter substance is still mainly enolic in character and is apparently a very complex condensation product of acetone and anthanthrone, since it is only partly soluble in boiling nitrobenzene and both soluble and insoluble fractions give characteristic colourations with alcoholic alkali. In a condensation of the type under consideration there is the possibility of the occurrence of chain reactions to be considered. Thus an acetone molecule that has condensed with a molecule of anthanthrone may, under the influence of the alkaline agent, comdense with another molecule of anthanthrone, and on this assumption the possibilities of further condensation is illimitable.

A condensation carried out by increasing still further the proportions of the other reagents with respect to anthanthrone proved that under these conditions a much higher proportion of this insoluble product was formed. 100 Gms. of acetone were dropped

into a stirred mixture of 1 gm. anthanthrone, 200 gms. anhydrous pyridine, and 10 gms. powdered potassium hydroxide maintained at 25°C. for 6 hours. The colour changes developed as in the previous experiment. On recovering the product as before, 1 gm. of a brown solid was obtained which produced a green colour with methyl alcoholic potassium hydroxide solution and a brownish solution with concentrated sulphuric acid.

The product was extracted with chlorobenzene and filtered cold as before. It was then extracted with boiling chlorobenzene and filtered hot. Only a small amount of solid dissolved in the hot solvent. The bulk of the material remained insoluble and when dry, gave a faint green colour with methyl alcoholic potassium hydroxide solution and a purple colour with concentrated sulphuric acid, which corresponds with the highly insoluble material obtained in the previous condensation. It was therefore evident that too vigorous conditions must not be employed or a very large amount of a product which is too complex for investigation is produced.

The yield of enolic products obtained in any of the previous condensations has been small. In an attempt to improve the yield, various experimental modifications were adopted. Carrying out the reaction in an atmosphere of nitrogen appeared to reduce resinification, but at most, 10% of enolic product was extracted with methyl alcoholic potassium hydroxide

solution. With the use of solid powdered potassium hydroxide as condensing agent the possibility of the reaction being a surface one was considered. With this in view a condensation was carried out in a bottle filled with glass balls and continuously rolled on mechanical rollers. This arrangement ensured an intimate mixture of the reactants and also prevented 'caking' of the potassium hydroxide.

A condensation was carried out in the bottle, using the quantities of the reagents which, from previous experience, appeared to produce the desired product in greatest yield. A mixture of 3 gms. anthanthrone, 100 gms. dry acetone, 200 gms. dry pyridine, and 20 gms. powdered and sieved potassium hydroxide were introduced and a blue-green colouration developed immediately. The mixture warmed up to about 25°C. and the bluish-green colouration persisted throughout 4 hours of agitation. On dilution with alcohol, cooling, and acidifying in the usual manner, 2·2 gms. of a brown solid were obtained. A trace of this solid gave an immediate deep green with cold methyl alcoholic potassium hydroxide solution.

The enolic content was extracted by warming to boiling point with N-methyl-alcoholic potassium hydroxide solution and filtering through two fine-pored filter papers. The dense green filtrate was run straight into dilute hydrochloric acid, the brown enolic

compound which precipitated was centrifuged, washed well with hot water, and dried. A 5·5% yield (0·12 gm.) of alkali soluble material was obtained by this means.

Anthanthrone is slightly soluble in hot methyl alcohol and the enolic product will therefore be contaminated by a small amount of unchanged anthanthrone. Further purification by means of chlorobenzene was therefore resorted to, with the following results.

1st Extract.

The 0·12 gms. of crude enolic compound was boiled with 10 ml. chlorobenzene. About one-third of the solid passed into solution. It was filtered hot and precipitated with 25 mls. of light petroleum. The brown precipitate was centrifuged off, washed with light petroleum, and recentrifuged. On drying, a trace of this substance gave a permanganate colour with golden fluorescence in concentrated sulphuric acid solution, and dissolved in methyl alcoholic potassium hydroxide to a blue solution with only the faintest trace of green.

2nd Extract.

The above extraction was repeated on the residue and the product gave a pure blue solution in methyl alcoholic potassium hydroxide. Concentrated sulphuric acid produced the same result as for the 1st extract.

3rd Extract.

By further extraction a product was obtained giving a pure blue colouration in methyl alcoholic potassium hydroxide solution, but with concentrated sulphuric acid a slightly more violet tint developed.

Most of the solid was continued in the first extract. The undissolved residue, about one-tenth of the original, gave a violet solution with concentrated sulphuric acid and also a pure blue with alcoholic potassium hydroxide solution.

Analysis of the above three fractions resulted as follows:-

1st Extract	2nd Extract	3rd Extract
C = 79·9%	C = 79·4%	C = 80·3%
H = 4·1%	H = 4·5%	H = 4·3%

Diacetonyl-anthanthrone requires C = 80·4, H = 4·3%, and the correspondence of the experimental figures with the calculated values led at first to the belief that a pure diacetonyl-anthanthrone had been isolated. The residue insoluble in hot chlorobenzene, producing as it does a violet solution in concentrated sulphuric acid, corresponds closely to the highly insoluble fraction isolated in previous experiments, and supports the contention that it consists of a more complex condensation product, or mixture of products derived from acetone and anthanthrone.

The behaviour of the supposed diacetonyl-anthanthrone extracted with methyl alcoholic potassium hydroxide solution and purified by means of chlorobenzene, in producing a blue potassium salt in methyl alcoholic potassium hydroxide solution represents a qualitative difference from previous preparations. The supposed diacetonyl-anthanthrone obtained in an earlier condensation (p. 19) gave a green colour in methyl alcoholic potassium hydroxide solution. Anthanthrone, however, imparts an orange tint to methyl alcohol and if the diacetonyl derivative, producing a blue potassium salt, is contaminated with a small amount of anthanthrone, a green tint will result. This is supported by the fact that the enolic product isolated in the condensation described on page 26 produced a green solution in methyl alcoholic potassium hydroxide, while on purification by means of chlorobenzene, the more soluble anthanthrone was removed and the purified product then gave a pure blue solution in methyl alcoholic potassium hydroxide.

Attempted Hydrolysis of Condensation Product.

Attention was now turned to the hydrolysis of the supposed diacetonyl-anthanthrone. A further condensation was carried out under the conditions described on page 25, and the enolic content extracted and separated. It was then refluxed with 100 mls. of 2 N-methyl-alcoholic

potassium hydroxide solution. The mixture developed a bluish-green colour immediately, the greenish tint probably being due to a little unchanged anthanthrone, since no chlorobenzene purification had been effected. After 15 hours heating, no colour change was noted. The alkaline solution was then made up to 3 N with potassium hydroxide pellets, and refluxing continued. After 40 hours the colour of the mixture was pure blue. It was evident therefore that some enolic compound was still present, so the solid was recovered by acidification, and refluxed with an acid mixture of 8 mls. glacial acetic acid, 4 mls. concentrated sulphuric acid, and 2 mls. of water. On first adding the acid mixture a violet-red solution was formed and no further colour change occurred during 40 hours of heating. The solid was then precipitated in water, centrifuged, washed, and dried. On dissolving a little of the brown solid in methyl alcohol and adding one drop of methyl alcoholic potassium hydroxide solution, a blue colouration developed. It was therefore evident that enolic compound was still present and that neither the alcoholic alkaline solution nor the acid mixture had effected complete hydrolysis.

This resistance of the acetonyl derivative is difficult to account for. The hydrolysis of 2-acetonyl-benzanthrone can be effected in 2 hours by heating with a 5% methyl alcoholic potassium hydroxide solution, by

which time the blue colouration has disappeared. In an earlier condensation, using anthanthrone (described on page 19), a product was isolated which produced a green colouration in 5% methyl alcoholic potassium hydroxide solution, and on heating under reflux for 2 hours with the same reagent, the green colour was almost wholly discharged, leaving only a green tinge. This would imply that the product isolated in the earlier condensation w as of a different nature to that obtained at a later date. So far no evidence has been obtained in support of this view, and a condensation carried out under the exact conditions described on page 17 failed to produce a more easily hydrolysable product. The enolic content of this latter condensation, after extraction with alcoholic alkali and purification by means of chlorobenzene, gave a product producing the same pure blue colour in methyl alcoholic potassium hydroxide solution as did the product obtained from later condensations. This product showed the same resistance to hydrolysis as did the product whose treatment by prolonged boiling with alcoholic alkali and with acid is described on the previous page.

Further Condensation Experiments with Acetone and Anthanthrone.

In order to study the hydrolysis of the acetonyl compound in greater detail and also to attempt to improve the yield, a new condensation was carried out,

modifying the conditions slightly. To a mixture of 3 gms. anthanthrone and 200 gms. anhydrous pyridine milled in a bottle with glass balls at room temperature, 25 gms. acetone and 5 gms. powdered potassium hydroxide were added. The mixture turned a bluish-green colour immediately and warmed slightly. Three further portions of 25 gms. acetone and 5 gms. powdered potassium hydroxide were added at hourly intervals until the mixture had been agitated for 4 hours. During this interval the colour of the mixture developed a more bluish tinge. The product was then recovered in the usual way and 3 gms. of a brown solid were obtained. Extraction of the enolic compound with successive portions of alcoholic alkali in the usual way resulted in 0·18 gms. of alkali soluble material being obtained corresponding to 6% yield.

The alkali soluble material was then extracted with four portions of 10 mls. hot chlorobenzene and precipitated by means of light petroleum. Fraction I contained about 0·1 gm. of material, and 0·02 gm. was completely insoluble in hot chlorobenzene. The solid from fraction I gave an initially green colour which was quickly masked by the usual permanganate tint with concentrated sulphuric acid, while fractions II, III and IV gave clean permanganate-coloured solutions with the same reagent. The greenish tint given by fraction I suggests that a little anthanthrone was present, and this is not unexpected, since large

volumes of methyl alcohol were used in the preliminary extraction. Anthanthrone is very sparingly soluble in methyl alcohol but tests showed that a definite colour was imparted to cold methyl alcohol shaken with some anthanthrone. Filtration through a fine-pored filter paper showed that the colour was not merely due to suspension of anthanthrone in the alcohol. Previous experience has shown, however, that anthanthrone is more soluble in chlorobenzene than the acetonyl compound, therefore rejection of fraction I obtained above should result in an enolic product free from anthanthrone.

This purified product obtained from fractions II, III and IV combined was boiled under reflux with a 3N methyl alcoholic potassium hydroxide solution. The cold alkaline solution was a pure blue colour and no colour change developed throughout 24 hours heating. A more vigorous treatment was then applied. The enolic product was recovered by acidifying and centrifuging, and it was then washed with a little methyl alcohol into a nickel crucible containing 5 gms. of potassium hydroxide pellets. Another 5 gms. potassium hydroxide were added and the crucible was heated in an oil bath at 180°C. The melt was stirred occasionally and the colour noted by the drop adhering to the stirrer. This colour was a deep blue at first and did not change during 4 hours heating.

At the end of four hours a test was made by

allowing a drop of the fusion mixture to solidify on the rod and dipping the solid into a little methyl alcohol. A blue colour developed immediately and indicated the continued presence of enolic compound. In a second test the rod with adhering solid was dipped into a little water to see if an alkali soluble carboxylic acid had been formed by the treatment. The solution turned a purplish tint. On boiling the aqueous alkaline solution, it immediately turned blue and on filtering the hot liquid, the blue particles were left on a fine-pored filter paper, the filtrate having a slight purplish tint. On acidifying the filtrate no colour change occurred but on acidifying the blue particles on the filter, the colour changed to purple. The blue was regenerated with aqueous sodium hydroxide. Thus a salt had been formed which appeared to be practically insoluble in water.

The alkali melt was then heated and maintained at 230°C. for 2 hours more, making 6 hours heating in all. It now had a purplish tint and on testing a little in methyl alcohol, a faint pinkish-violet colour developed with no trace of blue. Some further change had therefore occurred and the product was recovered by washing out the melt with water. The aqueous alkaline solution had a strong reddish-purple tint but some dark coloured solid remained undissolved. The mixture was then filtered, and on acidification of the filtrate, a

brown solid separated. A dark-coloured residue remained on the filter. Both the neutral and the acid solid fractions were too small for further investigation, hence the whole process was repeated with a further quantity of the purified enolic compound.

In this repeat experiment the melt was maintained at 230°C. for 6 hours in the hope of effecting a complete conversion of the enolic compound to the acid product. At the end of this period a test of the melt in methyl alcohol produced a reddish-violet tint. The melt was then washed out with water as before and the aqueous alkaline solution acidified. The whole of the solid was then separated in the centrifuge and repeatedly boiled with 2N aqueous sodium hydroxide until the alkaline solution was no longer coloured on filtration. About one-third of the solid did not dissolve in the hot aqueous alkali and the reddish-purple coloured filtrate deposited a brown solid on acidification. The residue, insoluble in hot aqueous alkali, was a very dark brown colour and dissolved with difficulty to a greenish-black solution in concentrated sulphuric acid. The acid fraction produced a greenish-brown solution.

Both of these fractions were too small for purification for analytical purposes, but the fact that a mixture of products was obtained on hydrolysis of the enolic compound is significant. It has previously

been shown that the enolic product of the condensation of acetone with anthanthrone gave analytical values after purification with chlorobenzene which correspond closely with those required by a diacetonyl-anthanthrone. The extreme measures necessary, however, to effect the hydrolysis of this product do not suggest that it is of such a simple nature. All through this work, fractions have been isolated which, on further investigation, have proved to be mixtures of anthanthrone derivatives of varying complexity, as was shown by their varying solubilities in organic solvents and slightly different colour reactions. This state of affairs can only be explained by assuming that chain formation proceeds in the condensation of acetone with anthanthrone. This complexity may be connected with the extreme resistance to hydrolysis of the acetonyl derivatives, and would also explain why a homogeneous product was not obtained on hydrolysis. If the starting compound was of a complex nature, cleavage in the presence of alkali might result in various ways with the production of a variety of products, and owing to the insoluble nature of these products, isolation and identification of pure individuals would be almost impossible.

Condensation in the Presence of Potassium Methoxide.

In an attempt to isolate a simpler condensation product of acetone and anthanthrone, a condensation was

carried out, using potassium methoxide as condensing agent. It was hoped that by the use of the milder alkaline agent, chain formation might be less prominent. 10 Gms. of acetone were added to a stirred mixture of 3 gms. anthanthrone, 200 gms. anhydrous pyridine, and 12·5 gms. dry freshly prepared potassium methoxide maintained at room temperature. The orange-red mixture turned green in 1 minute. No appreciable warming was observed. The colour of the mix ture gradually deepened to a greenish-blue and after 3 hours the mixture was diluted with 100 gms. ethyl alcohol, simultaneously cooled and acidified, and filtered. After washing, 2·45 gms. of dark brown solid were obtained. Traces of this solid produced a greenish-blue colour with methyl alcoholic potassium hydroxide solution, and dissolved to a green solution, with a trace of fluorescence, in concentrated sulphuric acid.

The enolic content was then extracted in the usual way with successive portions of cold methyl alcoholic potassium hydroxide solution and filtered immediately into dilute acid. In this way, after washing and drying the solid, 0·095 gms. of alkali soluble material were obtained corresponding to a yield of about 3½%. The alkali insoluble residue weighed 2·3 gms. and seemed to be mostly anthanthrone. The alkali soluble material was then extracted with 4 mls. hot chlorobenzene and filtered hot. Precipitation of the filtrate produced

a brown solid which was washed in the centrifuge and dried. The solid represented about 2/3 of the alkali soluble material. - Fraction I. The residue on the filter was then similarly treated with two 10 ml. portions of hot chlorobenzene and the hot filtered solution precipitated with light petroleum. Fractions II and III of the solid, weighing only a few milligrams, were thus obtained. About one-tenth of the enolic product remained insoluble in hot chlorobenzene. These fractions gave the following colour reactions:-

Fraction I.	Met. alc. KOH soln. -	Greenish-blue.
	Concentrated H_2SO_4. -	Reddish-purple solution with slight fluorescence.
Fraction II.	Met. alc. KOH soln. -	Blue.
	Concentrated H_2SO_4. -	Reddish-purple solution with slight fluorescence.
Fraction III.	Met. alc. KOH soln. -	) As for II.
	Concentrated H_2SO_4. -	)
Fraction IV.	Met. alc. KOH soln. -	Blue.
	Concentrated H_2SO_4. -	Purple solution with no fluorescence.

Fractions II and III were combined and heated ~~heated~~ under relux with 100 mls. of 2 N-methyl-alcoholic

potassium hydroxide solution. A blue colour developed immediately. Fraction I was treated similarly and a greenish-blue colour developed immediately, a trace of anthanthrone probably accounting for the green tint. Both of these solutions were heated for 24 hours, but no colour changes developed. This indicated that the products were extremely resistant to hydrolysis and that the milder alkaline agent had not produced a more easily hydrolysable product.

Condensation with all the Reagents in the Liquid Phase.

A further attempt was made to isolate a simpler condensation product of acetone and anthanthrone by carrying out the reaction under conditions such that all the reagents were in a single phase. This involved the use of methyl alcoholic potassium hydroxide solution, in which the potassium is mainly present as potassium methoxide, as condensing agent. It was realised that the presence of methyl alcohol during the condensation would probably introduce complications, but as a conclusion to the foregoing experiments, the attempt was justifiable.

By experiment it was found that 280 gms. of hot pyridine just held 0·9 gms. of anthanthrone in solution at the boiling point. 30 Mls. 2 N-methyl-alcoholic potassium hydroxide solution were added to the above solution and the mixture then assumed a purple colour.

To this mixture 20 mls. of acetone were added and the whole boiled under reflux. The colour of the mixture gradually turned more bluish until after 5 minutes a royal blue colour persisted. After heating for 35 minutes the mixture, which was still blue in colour, was acidified with 40 mls. 2 N-hydrochloric acid. The acid mixture was then dark brown. It was then filtered and a dark-brown solid separated from a dense brown filtrate. The solid was washed well with water and acetone, the washings from neither of which contained any appreciable amount of solid material. On drying, 0·65 gms. of dark-brown product were obtained. Traces of this substance gave a faint green colour with methyl alcoholic potassium hydroxide solution and dissolved to a deep-green solution in concentrated sulphuric acid.

The solid product was then finely powdered and extracted with successive 100 ml. portions of cold N-methyl alcoholic potassium hydroxide solution. The first extract had a faint green colour but the second and third extracts were practically colourless. On filtering into dilute acid, the total solid precipitated amounted to only a few milligrams and could not be separated. The material, insoluble in the alcoholic alkali, amounted to 0·6 gms. and was very dark brown in colour. It still dissolved to a green solution in concentrated sulphuric acid, but was only partially-soluble

in boiling monochlorobenzene. It therefore appeared to consist of unchanged anthanthrone, along with a more insoluble product. This latter insoluble fraction is most unlikely to be a methyl derivative produced by hydrolysis of acetonyl-anthanthrone because of its low solubility.

This condensation, in which all the reagents were in the liquid phase, has therefore failed to produce the desired result, namely, a simple condensation product of acetone and anthanthrone, and moreover, the yield of enolic product, under the conditions of the reaction, was negligibly small.

Summary of Acetone Condensations.

The results of the investigation of the condensation of acetone with anthanthrone may be summarised as follows:-

1. The condensation undoubtedly proceeds to some extent, since an enolic product is formed, under the described conditions, in yields up to a maximum of 12%.

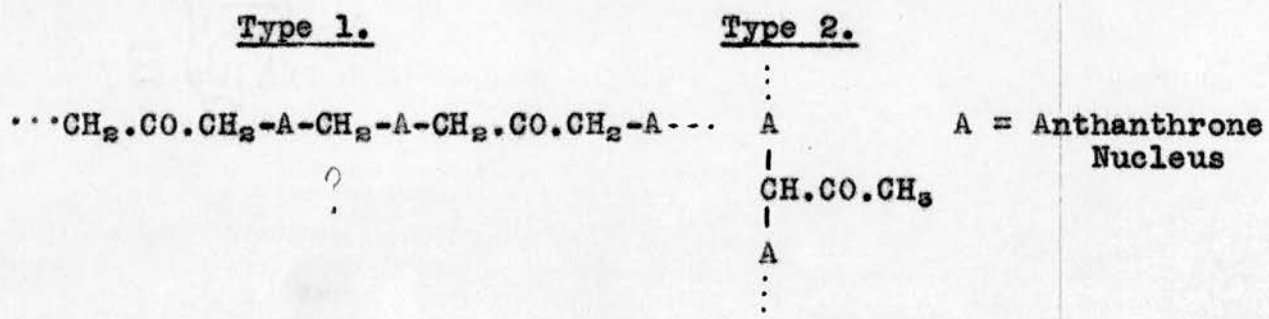
2. The condensation product is not homogeneous. A variety of compounds of varying complexity are obtained, apparently due to chain formation.

3. More vigorous conditions favour the formation of more complex products which are exceedingly insoluble.

4. The hydrolysis of any of the products isolated can only be effected under extreme conditions such as fusion with alkali, and the hydrolysis product is not homogeneous.

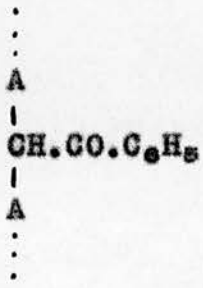
CONDENSATION Of ACETOPHENONE With ANTHANTHRONE.

The condensation of acetone with anthanthrone having yielded a series of products of varying complexity, apparently due to the ability of the simpler condensation products to condense further with themselves or with anthanthrone in a series of chain reactions, it was decided to investigate the possibility of condensing acetophenone with anthanthrone in the presence of an alkaline agent. Acetone has reactive centres at both ends of the molecule, while acetophenone possesses only one such centre. Two possible types of chain formation may go forward when acetone is condensed with anthanthrone, whereas the acetophenone molecule is capable of producing only one type. This may be illustrated as follows. Formations involving acetone and anthanthrone:-



The chain formation may even involve a combination of both these types but when acetophenone is condensed with anthanthrone, combination as shown by Type 1

become impossible. Combination as shown by Type 2 may occur as follows:-



A = Anthanthrone nucleus

The fact that, if condensation occurred, the chances of chain formation were lessened was, however, considered to merit an investigation being made of the condensation of acetophenone with anthanthrone.

Another factor must, of course, be considered. The phenyl group of the acetophenone molecule exerts an activating influence on the terminal - CH_3 group. This fact should facilitate condensation, but chain formation of type 2 may also be encouraged. Investigation of the process was, however, the only method of obtaining information on this point.

20 Gms. of acetophenone were run into a stirred mixture of 2 gms. anthanthrone, 134 gms. anhydrous pyridine, and 14 gms. of powdered potassium hydroxide maintained at 30°C. in a water-bath. The originally orange-red mixture became brownish and then greenish-brown until, after 3 minutes, the mixture was a deep-green colour. This deep-green colour persisted throughout 5½ hours stirring. The mixture was then diluted with alcohol, simultaneously cooled and acidified

and the reddish-brown mixture allowed to stand overnight. The mixture was filtered, and after washing well to remove pyridine and acetophenone, the dried reddish-brown solid weighed 2·9 gms. This solid gave a green colour with cold methyl alcoholic potassium hydroxide solution and dissolved to a blue solution, with strong red fluorescence, in concentrated sulphuric acid.

The product was then extracted with organic solvents as a preliminary separation. The solid was boiled with 150 mls. monochlorobenzene, cooled, and filtered. Precipitation of the filtrate with light petroleum yielded a brown solid which was filtered, washed free from solvent, and dried. Weight, 1·0 gm. - fraction I. The residue was then boiled with monochlorobenzene and filtered hot. The filtrate was precipitated with light petroleum and the brown solid separated as before; weight, 0·4 gms. - fraction II. This extraction was repeated with o-dichlorobenzene as solvent and a further quantity of dark brown solid obtained: weight, 0·5 gm. - fraction III. 0·5 Gms. of solid remained insoluble in latter solvent - fraction IV. These fractions were investigated separately.

Fraction I. A trace dissolved to a greenish-blue solution, with red fluorescence in concentrated sulphuric acid, and a green colour was produced with

methyl alcoholic potassium hydroxide solution. This solid seemed to consist of unchanged anthanthrone along with a little enolic compound.

Fraction II. A trace dissolved to a purple solution with weak red fluorescence in concentrated sulphuric acid, and produced a green colour with methyl alcoholic potassium hydroxide solution.

Fraction III. The solid produced the same colour reactions as for fraction II.

Fraction IV. The solid produced a purple solution with strong red fluorescence in concentrated sulphuric acid, and a green colour with methyl alcoholic potassium hydroxide solution.

It was then proposed to treat each of the above fractions separately by boiling for 5-10 minutes with normal methyl alcoholic potassium hydroxide solution and filtering directly through two fine-pored filter papers into dilute hydrochloric acid. This was attempted first with fraction II. On heating the alcoholic alkaline solution with the solid, a clear green colour developed immediately, but it was observed that the clear green quickly faded to a dark brownish-green tint. It therefore appeared that the product was readily attacked by the alcoholic alkali. A little of this greenish-brown solution was acidified with dilute sulphuric acid, diluted, and boiled until all the salts were in solution. The mixture then had the

characteristic odour of benzoic acid and of methyl benzoate produced by further interaction with methyl alcohol. This confirmed that hydrolysis was taking place with the production of benzoic acid as by-product by cleavage of the acetophenonyl derivative. The original idea of effecting a separation was therefore discarded and an estimation of the amount of benzoic acid formed on complete hydrolysis of a weighed portion of the product attempted. Since the solid composing fraction II had already been used in the attempt to extract the enolic compound by means of methyl alcoholic potassium hydroxide solution, this experiment was carried out on the solid of fraction III, i.e., that extracted by means of hot o-dichlorobenzene.

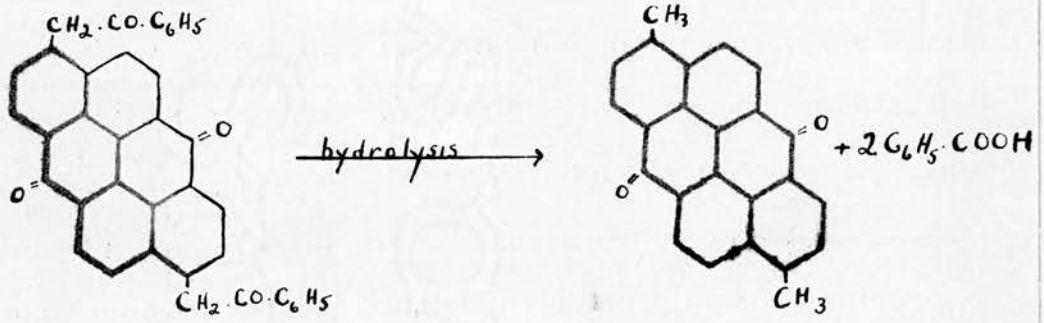
A weighed amount of the solid was boiled under reflux with a measured quantity of methyl alcoholic potassium hydroxide solution in a resistance glass flask until the green colouration had been completely discharged. This required 6 hours and the mixture was then brown. The residual alcoholic alkali was then estimated by titration with 0·1 N sulphuric acid solution. A correction was applied for a small amount of acid present in the methyl alcohol. The results obtained were as follows:- 0·3077 Gms. of the solid required the equivalent of 10·42 mls. 0·1 N methyl alcoholic potassium hydroxide for complete hydrolysis.

Now 1 litre N. met. alc. KOH soln. ≡ 122 gms. benzoic acid.

∴ 10·42 mls. 0·1 N. met. alc. KOH soln. ≡ 0·1271 gms. benzoic acid.

∴ 0·3077 gms. of the acetophenonyl derivative produce 0·1271 gms. of benzoic acid on hydrolysis.

By calculation the amount of benzoic acid formed on complete hydrolysis of 0·3077 gms. pure diacetophenonyl-anthanthrone should be 0·1385 gms. The experimental value of 0·1271 gms. represents 92% of this amount and thus approximates to the value required for a disubstituted acetophenone derivative of anthanthrone.

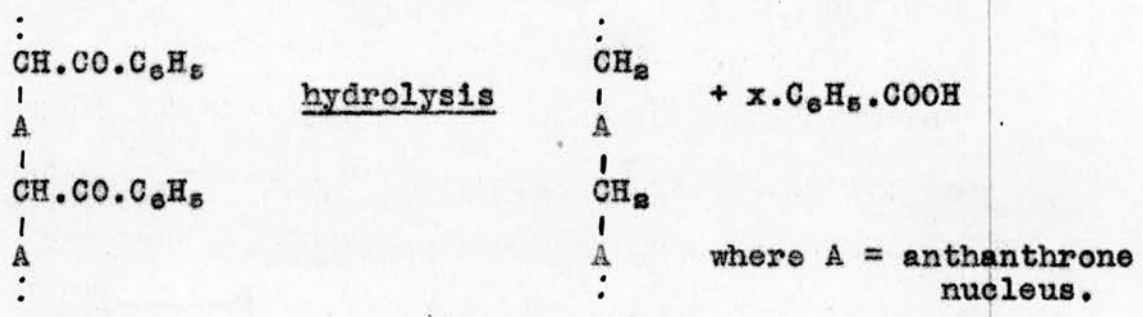


Diacetophenonyl-anthanthrone. Dimethyl-anthanthrone.

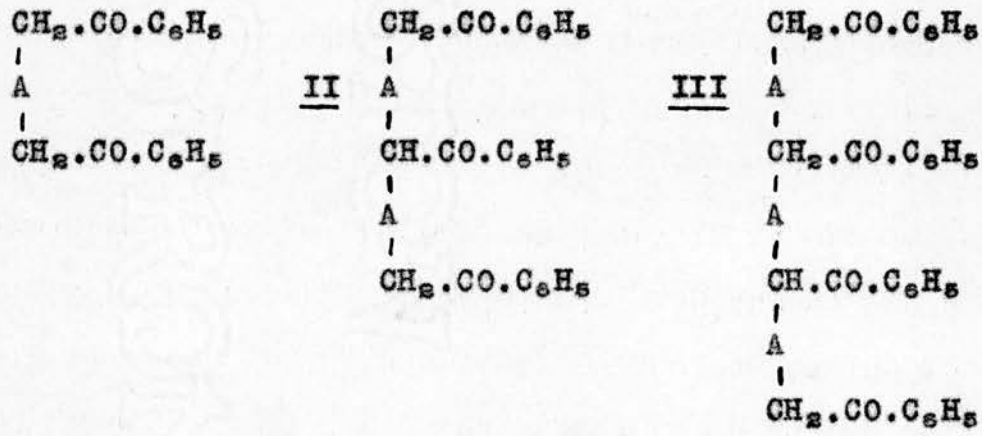
As was expected, the residue after hydrolysis produced no colour with methyl alcoholic potassium hydroxide solution but still dissolved to a blue solution in concentrated sulphuric acid. The solid dyed cotton a pleasing brown shade from a violet-red vat. The remainder of the hydrolysis product was boiled with 60 mls. monochlorobenzene and filtered hot. About one-quarter of the solid passed into solution and

the filtrate, on precipitation with light petroleum, yielded a brown solid which was thoroughly washed, dried, and analysed. The following values were obtained: C = 81·8, H = 3·31%. The values required for a dimethyl-anthanthrone are C = 86·2, H = 4·19%. The experimental values obviously do not agree with the calculated values and the assumption that a condensation product of a simple type had been isolated must be abandoned. Several other observations tend to confirm the view. The assumed dimethyl-anthanthrone produced a blue solution in concentrated sulphuric acid. Anthanthrone itself produces a green solution and the dimethyl derivative would not be expected to differ greatly in properties from those of the parent compound. This same reasoning applies to the relative insolubility, as compared with anthanthrone, of the presumed dimethyl compound in hot monochlorobenzene. Anthanthrone is comparatively soluble in this solvent, while only one-quarter of the total of the presumed dimethyl derivative passed into solution in 60 mls. of hot monochlorobenzene. This evidence, along with the fact that the primary product of the condensation also appeared to consist of a mixture of compounds of varying solubility, proves that chain formation has not been eliminated.

This chain formation will be of the second type as was indicated previously. Thus a complex may be formed as follows:-



This complex, however, may be quite sensitive to alkali but would still produce a complex derivative on hydrolysis. The amount of benzoic acid produced on hydrolysis would vary according to the length of the chain. Thus for the first three members of the above series, 100 gms. of each would produce the following amounts of benzoic acid on hydrolysis:-

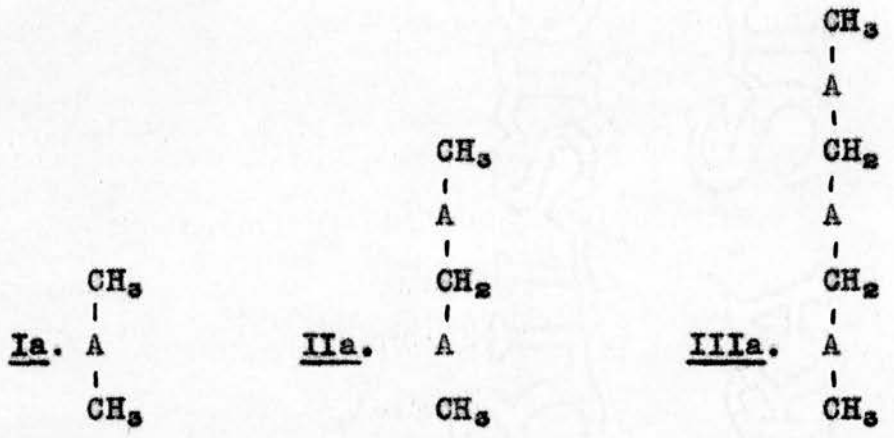


100 Gms. of compound I, on hydrolysis, yields 45·0 gms. of benzoic acid.

100 Gms. of compound II, on hydrolysis, yields 38·0 gms. of benzoic acid.

100 Gms. of compound III, on hydrolysis, yields 35·2 gms. of benzoic acid.

From the results actually obtained with a small amount of product 100 gms., hydrolysed as described on page 45, would produce 41·3 gms. of benzoic acid. This value lies between the calculated valuesof compounds I and II and lends credence to the belief that the product is not of the simpler composition. The analysis values for the hydrolysis products corresponding to the aceto-phenonyl derivatives shown above are as follows:-



C = 86·2%
H = 4·19%

C = 86·5%
H = 3·68%

C = 86·6%
H = 3·50%

Here again comparison with the experimental values obtained for the hydrolysed acetophenonyl derivative of anthanthrone (C = 81·8, H = 3·31%) shows an agree-ment in the lower hydrogen values, indicating a more complex hydrolysis product, although no correspondence with carbon value is shown.

Modified Condensation of Acetophenone and Anthanthrone.

A second condensation, cutting down the time of contact of the reagents and also employing the milling process at room temperature, was carried out in the hope of isolating some simpler condensation product.

20 Gms. acetophenone, 2 gms. anthanthrone, 134 gms. anhydrous pyridine, and 15 gms. powdered potassium hydroxide were mixed in a bottle with glass balls and rolled on mechanical rollers at room temperature. The mixture immediately developed a deep green colour and remained so throughout 3½ hours of agitation. No appreciable rise in temperature of the contents of the bottle was noted at any time. The mixture was diluted with 60 gms. of ethyl alcohol and simultaneously cooled and acidified. The reddish-brown mixture was filtered and the reddish-brown solid washed well with water, alcohol, and ether. The dried solid weighed 2·6 gms.

The solid was then finely-powdered and 1 gm. of it shaken with 100 mls. of cold N-methyl-alcoholic potassium hydroxide solution. The green solution was quickly filtered into dilute hydrochloric acid solution. In this way the time of contact of the enolic compound with the alcoholic alkali was kept as short as possible. Similar extractions were carried out until the filtrate had only a faint green tint. The brown solid which separated on acidification was centrifuged, thoroughly

washed with hot water, and dried. The 0·14 gms. of enolic product obtained in this way correspond to a 14% yield. A trace of this solid dissolved to a blue solution with strong red fluorescence in concentrated sulphuric acid. The residue, insoluble in the alcoholic alkali, dissolved to a green solution in concentrated sulphuric acid and appeared to consist mainly of unchanged anthanthrone.

The 0·14 gms. of enolic compound obtained above was extracted with four successive portions of 10 mls. hot monochlorobenzene, and the solid precipitated from each extract with 25 ml. portions of light petroleum. In this way, four fractions of dark-red solid were obtained, fraction I being most soluble in hot chlorobenzene, and fraction IV least so. Fraction I contained most solid and fraction IV was negligible in bulk. A small amount of solid was completely insoluble in the hot chlorobenzene. Samples of each fraction produced a blue colour with concentrated sulphuric acid with only a trace of fluorescence. Fractions III and IV were combined and an analysis of the fractions carried out, with the following results:-

Fraction I.	Fraction II.	Fraction III IV.
C = 80·8%	C = 79·0%	C = 79·3%
H = 3·34%	H = 3·50%	H = 3·60%

In spite of the correspondence in the analyses of

fractions II and (III and IV), the products do not conform to the value required for a diacetophenonyl-anthanthrone. The analyses values for the series of acetophenonyl derivatives of anthanthrone shown on page 48 are as follows:-

I	C = 84·11% H = 4·06%	II	C = 84·65% H = 3·73%	III	C = 84·85% H = 3·61%

A comparison of these analyses values with the experimental results again indicates, by the low hydrogen values of the latter, that the derivatives isolated are not of a simple nature. It therefore appears that, as before, more complex derivatives are being formed by a chain mechanism, and that a mixture of these products is produced in the condensation.

CONDENSATION Of BENZYL CYANIDE And ANTHANTHRONE.

Test-tube experiments carried out on a mixture of anthanthrone, pyridine, benzyl cyanide, and powdered potassium hydroxide indicated that reaction occurred with these reagents at room temperature. The condensation of benzyl cyanide with benzanthrone is described in B.P. 319,593, and it is there stated that the reaction goes forward readily at 10-15° C. in an atmosphere of nitrogen with stirring for 2-3 hours. A condensation was attempted on similar lines with 3 gms. anthanthrone, 27 gms. dry pyridine, 10 gms. powdered potassium hydroxide, and 10 gms. benzyl cyanide. The benzyl cyanide was dropped into the stirred mixture maintained at 15-20°C. The initially orange-red mixture immediately turned a dark green and this colour persisted throughout 3 hours stirring. The reaction mixture was then diluted with 40 gms. ethyl alcohol, and the still green mixture poured into an excess of dilute hydrochloric acid cooled by addition of ice.

Filtration yielded a very dark-red solid which was washed with water and then triturated with alcohol to remove unchanged benzyl cyanide and some resinous material. 2·5 Gms. of a red solid were then obtained.

A test portion dissolved in concentrated sulphuric acid to a blue solution with crimson fluorescence, and gave a green solution with methyl alcoholic potassium hydroxide solution, which deepened in colour on warming.

Before resorting to purification by means of organic solvents or to extraction of the alkali-soluble content by means of methyl alcoholic potassium hydroxide solution, an attempt was made to hydrolyse the mixture in the hope of isolating a carboxylic acid by hydrolysis of the nitrile grouping.

(a) A little of the solid was boiled under reflux with a mixture of 8 mls. glacial acetic acid, 4 mls. concentrated sulphuric acid, and 2 mls. of water. This mixture was blue at first but, on heating, a reddish-purple colour developed, and this colour persisted throughout 24 hours heating. After 2 hours, a little of the mixture was precipitated in water and a reddish-purple solid deposited. This test portion was completely insoluble in cold aqueous alkali and none dissolved, even on heating. A similar result was obtained on recovery of the solid after 24 hours heating. This solid, however, then gave a violet-blue colour with concentrated sulphuric acid and no colour with methyl alcoholic potassium hydroxide solution. Some chemical change therefore had been effected by the treatment. The quantity recovered was insufficient for testing for the presence of nitrogen.

(b) Meanwhile a little more of the reaction mixture was boiled with methyl alcoholic potassium hydroxide solution. The solution was coloured green at first but gradually became yellowish, and after several hours was brown. The solid recovered by acidification dissolved to a violet-blue solution in concentrated sulphuric acid and was not soluble in aqueous alkali. A change similar to that effected by the acid treatment therefore appears to have occurred, but no acid product was detected.

A new condensation was next attempted, employing the milling process in a nitrogen-filled bottle. A mixture of 3 gms. anthanthrone, 100 gms. anhydrous pyridine, 10 gms. powdered potassium hydroxide, and 10 gms. benzyl cyanide were rolled in a bottle with glass balls and with the air displaced by nitrogen. The colour changes were similar to those observed in the previous condensation, and on first mixing the components, the mixture warmed to about 30°C. After 4 hours the mixture was diluted with 40 gms. of ethyl alcohol and the solid recovered in the usual way. On removing excess benzyl cyanide and resinous matter by washing with acetone, 3·2 gms. of a red solid were obtained.

The solid was extracted with successive portions of 100 mls. normal methyl alcoholic potassium hydroxide

solution at the boiling point and the dark-green solution filtered through two fine-pored filter papers directly into dilute hydrochloric acid solution. The first 250 mls. of alcoholic alkaline solution were deep-green and were collected separately (A). The filtrate then became a weaker green colour and a brown tint developed. The next 100 mls. were therefore also collected separately (B). The succeeding alcoholic potassium hydroxide filtrates were very weak green in colour and the solid recovered from them was too small in bulk to be investigated. The undissolved residue no longer gave a green tint in methyl alcoholic potassium hydroxide solution and amounted to 2·45 gms. A trace of the residue dissolved in concentrated sulphuric acid to a dark bottle-green coloured solution and appeared to be mainly unchanged anthanthrone. Fractions (A) and (B) were then investigated separately.

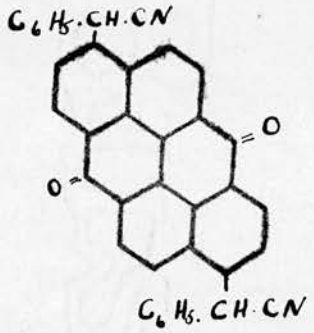
Fraction (A).

On filtration of the acidified solution, 0·53 gms. of a deep reddish-purple solid were obtained and the filtrate was an indigo-blue colour. The colour of the filtrate was not changed in tint by addition of potassium hydroxide or of hydrochloric acid. The solid was warmed with 10 mls. chlorobenzene, cooled, and filtered, yielding 0·18 gms. of material (I). The filtrate from the latter was blood-red and was treated with an equal volume of light petroleum, yielding 0·12 gms.

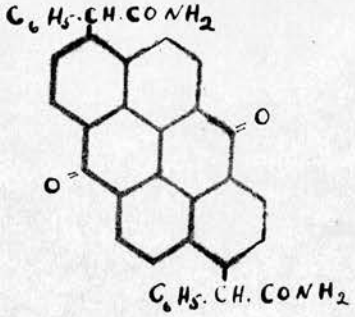
of a deep-red solid (II). Further precipitation of the filtrate with petroleum gave 0·16 gms. of reddish material (III). These fractions were dried and analysed with results as follows:-

I - C = 79·6, H = 4·1, N = 3·2%. - Least soluble fraction.
II - C = 82·2, H = 3·9, N = 4·2%.
III - C = 82·3, H = 4·0, N = 4·1%. - Most soluble fraction.

A di-benzylcyano-anthanthrone would require C = 85·07, H = 3·73, N = 5·22%.



Despite the similarity in the analyses of (II) and (III), the products did not appear to conform to any of the expected formulae and were assumed to be mixtures containing an anthanthronyl-αα'-diphenyl-diacetic-diamide (i.e., containing two $C_6H_5.CH.CONH_2$ groupings linked to an anthanthrone nucleus) or more complex condensation products of this type, together with a little anthanthrone. The diamide of the following structure



would require C = 79·72, H = 4·20, N = 4·90%, and anthanthrone would require C = 86·30, H = 3·30%. The analysis figures obtained for fractions (II) and (III) above are consistent with such a mixture.

Fraction (IIA) and (IIIA) were then combined and the hydrolysis of the product attempted. The solid was heated with methyl alcoholic potassium hydroxide solution in a current of air, the latter being probably without special effect. The green colour changed to a brown in 3 hours, and since the potassium salt formed appeared to be very difficultly soluble, 25% of water was added. A permanganate-purple colour developed on continuing heating, and the colour showed no further change after heating for 17 hours in all.

The permanganate-coloured suspension was diluted and digested on the water-bath, and the suspension of dark-purple solid was filtered at the pump. The residue and filtrate were examined as follows:-

Residue. The solid, after again being boiled with water and washed on the filter, gave 0·0664 gms. of a neutral dark purplish-black product. This product gave a purple-brown colour with concentrated sulphuric acid, but did not dissolve readily. It is therefore probably very complex. A trace treated with cold methyl alcoholic potassium hydroxide solution produced no colour change, but a very faint purplish tinge appeared on boiling. This colour may be due to a

trace of the neutral product dissolving in the hot methyl alcohol as solvent. Analysis figures obtained for this product (C = 77·47, H = 4·39%) were, however, valueless, as about 10% of residue was left after combustion, despite the prolonged washing to which the solid had been subjected.

Filtrate. On acidification of the filtrate, a red acidic product separated which, on being filtered, washed and dried, gave 0·0665 gms. of dark-red solid. A trace of this substance produced a dark bottle-green colouration with concentrated sulphuric acid. Only a small fraction of the solid could be removed by extraction with boiling monochlorobenzene; further small amounts were removed by boiling with o-dichlorobenzene and carbitol successively. Nearly one-third of the solid was insoluble, even in these solvents.

The monochlorobenzene solution, on precipitation with petroleum, gave 0·0078 gms. of a dark-red solid. This solid now gave a brown solution with greenish tinge in concentrated sulphuric acid. The solid was unfortunately lost before an analysis could be carried out. The fraction insoluble in monochlorobenzene o-dichlorobenzene ~~o-dichlorobenzene~~, or carbitol, which amounted to 0·0184 gms., dissolved to a clear green solution in concentrated sulphuric acid. Analysis figures obtained for this product (C = 71·13, H = 4·50%) were again valueless owing to a very large residue,

about 25 per cent, being left after combustion.

The solubility results again point to the formation of a mixture of complex condensation products resembling in this respect those obtained with acetone and and anthanthrone.

An investigation into the nature of the residues obtained on combustion for analysis of the products obtained from the hydrolysis described above was carried out. Potassium having been found absent, silica from glassware was thought to be the most likely source of the residues, so the following test, depending on the formation of silico-molybdate was carried out:-

A portion of the product insoluble in carbitol was ignited on a platinum foil until all carbonaceous matter was eliminated. The residue was then fused with a small quantity of sodium carbonate and the mixture dissolved in water. Dilute nitric acid was then added until the solution had p_H approximately equal to 1. (This was done with thymol blue indicator paper). Two drops of a 10% solution of ammonium molybdate were then added. The mixture then had a faint yellow colour, showing the presence of silico-molybdate. Comparison of this mixture with a blank and with a solution in which a known amount of sodium silicate was present indicated that silica was present in the test portion in very small amount. The test does, however, confirm that silica is interfering with

the analyses.

Fraction (B) (page 56).

On acidification of fraction B of the methyl alcoholic potassium hydroxide solution, 0·18 gms. of a red solid were obtained, the acid filtrate being colourless. This solid on analysis gave C = 82·2, H = 3·60, N = 2·50%. These figures are consistent with a mixture such as was obtained from fraction A, but containing more anthanthrone.

Condensation of Benzyl Cyanide and Anthanthrone at 100°C.

The foregoing condensation of anthanthrone and benzyl cyanide, carried out by milling the reagents in a bottle at room temperature, resulted in about 82% of the anthanthrone being recovered unchanged after extraction of the acidic product with methyl alcoholic potassium hydroxide solution. It was therefore decided to investigate the effect on the reaction of treating the components at a higher temperature, even though a rise of temperature in the case of anthanthrone and acetone had been found to yield an extremely complex and unworkable product.

10 Gms. of benzyl cyanide were dropped into a stirred mixture of 3 gms. anthanthrone, 100 gms. anhydrous pyridine, and 10 gms. of powdered potassium hydroxide maintained at 100°C. in a water-bath and in a nitrogen atmosphere. The mixture became green

immediately and remained a deep-green throughout 3 hours stirring. The product was then diluted with alcohol and acidified in the usual manner. On allowing the mixture to stand overnight, the solid separated as a resinous mass from which the acid liquid could be poured. The mass was washed into a filter with acetone and the whole washed very thoroughly with that solvent. A reddish-purple coloured solid was obtained which, when dry, weighed 1·70 gms. (The large discrepancy from 3 gms. of starting material must be due to loss during washing with acetone, although no solid matter was deposited from the diluted wash liquor). Traces of this solid gave a deep-green colour with methyl alcoholic potassium hydroxide solution and dissolved to a blue solution with crimson fluorescence in concentrated sulphuric acid.

The whole solid was then extracted with successive 100 ml. portions of cold normal methyl alcoholic potassium hydroxide solution, and filtered immediately into dilute aqueous hydrochloric acid. The reddish precipitate which appeared was centrifuged, washed thoroughly with hot water, and dried. This solid weighed 0·26 gms. so that increasing the temperature at which the reaction was carried out did not result in an increased yield of alkali-soluble product. This lowered yield may be due to the alkali attacking the the benzylcyano-anthanthrones at the higher temperatures

and converting them partly into the corresponding amides, which would not dissolve in alcoholic alkali.

The residue remaining after extraction with alcoholic alkali was then washed into a filter with dilute hydrochloric acid and thoroughly washed with water. After drying, this solid weighed 1·3 gms. Small-scale tests showed that it differed from anthanthrone in that a part of it was readily soluble in cold ethyl alcohol to form a purple solution. It was therefore extracted exhaustively with this solvent. After evaporating the alcohol filtrate to dryness, 0·71 gms. of a reddish-purple solid were obtained. A trace of this solid dissolved to a clean blue solution in concentrated sulphuric acid, and on adding a drop of methyl alcoholic potassium hydroxide solution to a trace dissolved in methyl alcohol, the pink solution changed to a brown tint. This faint brown colour is also observed when the green solution of benzylcyano-condensation products in alcoholic alkali is heated, and may correspond to the amide stage of hydrolysis. The fraction insoluble in cold ethyl alcohol weighed 0·35 gms. and gave colour reactions with alcoholic alkali and concentrated sulphuric acid identical with those of the alcohol-soluble fraction. Hence the undissolved fraction has not the properties of unchanged anthanthrone.

The alcohol-soluble product obtained above softened at 230°C. and did not melt completely up to

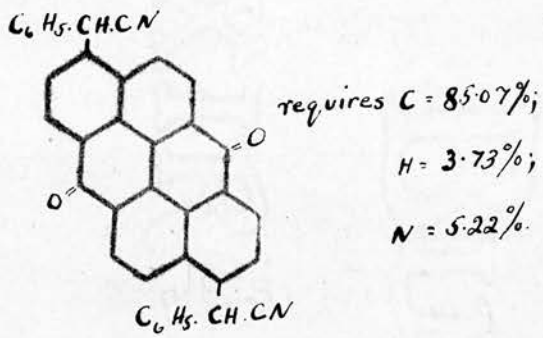
320°C. Tested qualitatively it was found to contain a small amount of nitrogen as also was the product insoluble in cold ethyl alcohol. The alcohol-soluble material was also found to be partly soluble in hot benzene. A further purification was therefore attempted, using this solvent.

0·3 Gms. of alcohol-soluble material was boiled with 60 mls. of benzene and filtered hot (extract I). A moderate amount (0·05 gms.) of dark residue remained on the filter. The benzene solution was deep red with a purplish tint and was fluorescent. Two more extractions (extracts II and III) were made of the residue on the filter with two portions of 40 mls. hot benzene.

Extract I was evaporated to half bulk and still held most of the solid in solution. It was then boiled, filtered hot through a fine paper, and precipitated with twice its volume of light petroleum. The red solid which appeared was filtered off and dried. It weighed 0·07 gms. This solid gave a reddish-purple non-fluorescent solution when a trace was dissolved in concentrated sulphuric acid, and produced no colour with methyl alcoholic potassium hydroxide solution. The filtrate from this extraction, on evaporation to dryness, was found to contain about 0·1 gms. of red solid.

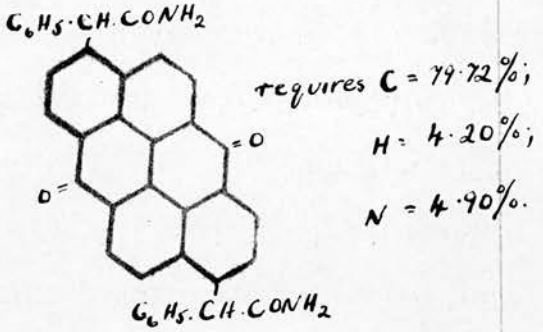
Extracts II and III were united and precipitated with light petroleum, but the amount of solid obtained was too small to work with. The weight of substance

insoluble in hot benzene was 0·05 gm. Analysis of fraction I resulted in the following values:- C = 82·12, H = 3·15, N = 1·23%. These values do not approximate to those of any of the expected anthanthrone derivatives such as the di-benzylcyano or di-amide derivatives shown:-



requires C = 85·07%;
H = 3·73%;
N = 5·22%.

Di-benzylcyano derivative.



requires C = 79·72%;
H = 4·20%;
N = 4·90%.

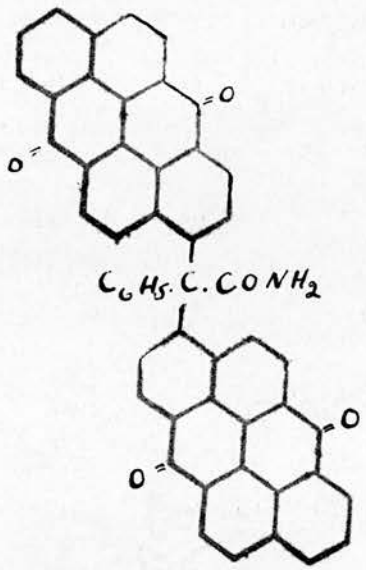
Di-amide derivative.

The experimental nitrogen value is much too low for either of these derivatives. The analytical values required for the corresponding mono-substituted anthanthrones are as follows:-

Mono-benzylcyano derivative requires C = 85·51, H = 3·56, N = 3·32%.

Mono-amide derivative requires C = 82·0, H = 3·87, N = 3·19%.

In these cases the nitrogen values, though closer, are still too high. A compound of the following type corresponds to the low nitrogen value obtained, but in no way would account for the solubility of the compound in cold ethyl alcohol:-



This complex requires C = 84·0, H = 3·36, N = 1·88%.

The remaining 0·4 gms. of the ethyl alcohol soluble material was refluxed with 100 mls. normal methyl alcoholic potassium hydroxide solution with a current of air passing through the mixture. The mixture was brown at first but after 9 hours refluxing a purple colour developed. Heating was continued for a further 6 hours and the mixture then filtered through two fine-pored papers, when a black solid was separated from a purplish-red filtrate. The solid was washed with very dilute aqueous alkali and then with hot water until it was free from salts. On drying, the solid weighed 0·3 gms.

This presumed hydrolysed derivative was then examined. Tests showed that a small amount of nitrogen

was still present. The solid was therefore left in contact with a normal solution of methyl alcoholic potassium hydroxide for 72 hours. On recovery of the solid and again testing, a small amount of nitrogen was still found to be present. Hydrolysis was apparently incomplete and a separation was then attempted, using an aluminium oxide adsorption tube. A tube, 18 inches long and 1 inch in diamter, was set up and packed with aluminium oxide, using benzene for elution. 0·1 Gm. of the material containing a small amount of nitrogen was shaken with benzene and the mixture filtered; 0·075 gm. dissolved to a red fluorescent solution, 0·025 gm. of the solid being insoluble in benzene.

The solution was run into the adsorption tube and the adsorption layer developed by washing with benzene. A reddish forerunner ran right through the tube (I). Next came the main orange-red band, which was eventually washed through the tube and collected separately as a red fluorescent benzene solution (II). A brownish-red band, which remained at the top of the tube, probably contained a very complex mixture (III). The main benzene fraction (II) was evaporated to dryness and 0·053 gm. of red solid was recovered which, on testing, was found to contain a small amount of nitrogen. This solid dissolved to a dark-green solution in concentrated sulphuric acid and, on analysis, gave the values C = 82·1, H = 4·44, N = 1·66%.

The alkaline filtrate from the attempted hydrolysis of the alcohol soluble product was next examined. On acidification with dilute aqueous hydrochloric acid, a very small amount of a bright-red acid separated. This solid was thoroughly washed with hot water in a centrifuge. The dried product dissolved to a deep-green solution in concentrated sulphuric acid. Analysis of this acid product gave the following values:- C = 73·64, H = 3·54%, after correction for 1% of incombustible residue.

The above processes may be summarised as follows.

Anthanthrone

+KOH, pyridine, and benzylcyanide

Mixture of products (resinous)

Washed with acetone

Reddish-purple solid, 1·7 gm.

Extracted with methyl alcoholic KOH soln.

Reddish alkali soluble material, 0·26 gm.

Alkali insoluble material, 1·3 gm.

Extracted with cold ethyl alc.

Soluble fraction 0·71 gm.

Insoluble fraction, 0·35gm.

0·4 Gm. treated met.alc. KOH soln.

Filtered after 15 hrs. heating.

Small amounts of red acid product C.
Analysis: C=73·64%
H= 3·54%

Nautral product, 0·2 gm.

Left in contact with met. alc. KOH soln. for 72 hrs. × filtered. Solid dissolved in benzene × separated in Al_2O_3 tube.

I
Small content

II
0·053 g. red solid B.
Analysis: C=82·1%
H= 4·44%
N= 1·66%.

III
Small amount

0·3 Gm. fractionally extracted with hot benzene

Precipitated with light petroleum

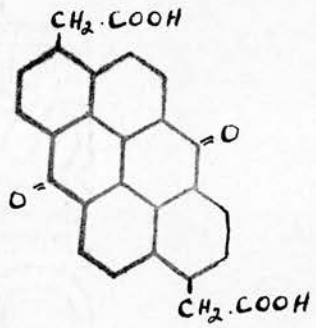
Fraction insoluble in hot benzene, 0·05 gm

I
Red solid, 0·07gm.
Analysis: C=82·12%
H= 3·15%
N= 1·23%

II
A. Very small

III

The analyses values for the neutral product B recovered after attempted hydrolysis of the alcohol-soluble material show a striking similarity to those for the alcohol-soluble material A fractionally extracted with benzene. This suggests that the treatment by heating with alcoholic alkali has left the bulk of the product unchanged. The values C = 73·64, H = 3·54%, for the acid product C formed by hydrolysis correspond moderately closely to those required by an anthanthrone-diacetic acid of the following constitution:-



This derivative would require C = 73·93, H = 3·32%. The formation of such a compound, however, postulates the loss of the phenyl group of a benzylcyano compound, which is not a usual change, as it is more probable that the carboxyl group would lose carbon dioxide.

The analysis values for the neutral product B after treatment with methyl alcoholic potassium hydroxide solution agree with none of the simpler anthanthrone derivatives - for example, a mono- or di-benzylcyano-anthanthrone or a mono- or di-amido derivative. Values for these latter compounds are

quoted on page 65. The lower nitrogen value, 1·66%, obtained on analysis of the compound under consideration, suggests that a complex such as a di-anthanthronyl-phenyl-acetamide has been isolated as was described on page 66. Here again, however, it is difficult to reconcile the relatively high solubility of the product with its complexity.

A study of the products obtained from the condensation of benzyl cyanide with anthanthrone, therefore, has revealed that the isolation of simple homogeneous derivatives is a matter of extreme difficulty. At room temperatures, complex mixtures have been produced, and separation of the products, as far as possible by means of organic solvents, has yielded fractions which are strongly resistant to acid hydrolysis. An alkali-soluble fraction can, however, be isolated from the crude condensation mixture which is rapidly attacked by hot methyl alcoholic potassium hydroxide solution, giving a product which is no longer appreciably soluble in alcoholic potassium hydroxide solution and which gives no blue or green colour but only a faint-brown with this reagent. Further, it still contains nitrogen. This reaction appears to correspond to the conversion of a benzylcyano to an amide derivative, although analytical confirmation of this could not be obtained.

When formed at 100°C. the condensation product contains a considerable fraction which is much more

soluble in organic solvents and presumably is less complex, possibly because the derivative initially formed on the surface of the potassium hydroxide particles rapidly undergoes further change at the high temperature and in contact with the alkali, in such a manner that it is no longer readily attacked by more benzyl cyanide. But even in this case a complicated mixture was produced, and no homogeneous compound could be isolated.

The possibility of a pyridino-compound having been isolated in any of the foregoing condensations was not overlooked, but this appears to be excluded by the following considerations:-

(a) No basic product was ever detected in the anthanthrone condensations.

(b) In an attempt to condense anthanthrone with formamide (see page 77), over a period of four hours, the recovered product contained no nitrogen and gave a completely colourless acid filtrate.

Moreover, pyridine is recommended in the original patent for use in condensations involving benzanthrone.

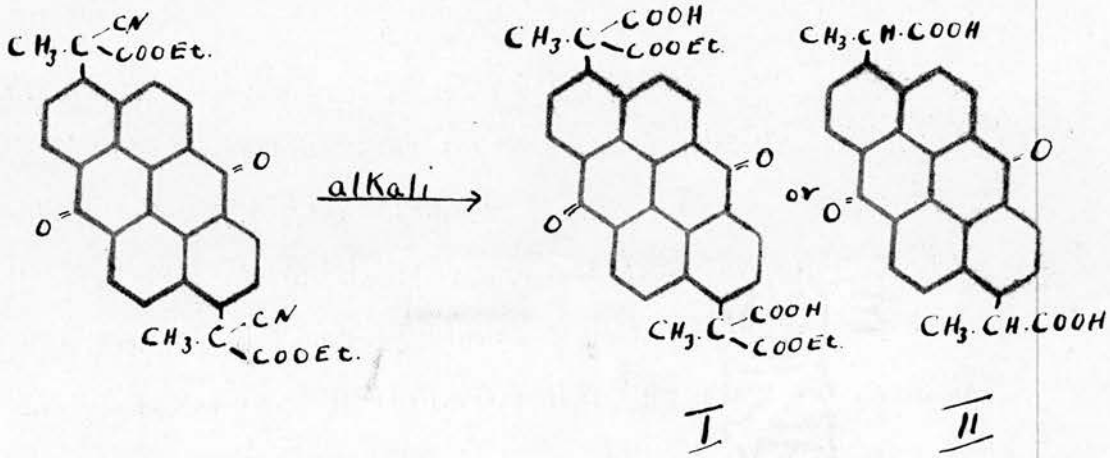
CONDENSATION Of α-CYANOPROPIONIC ESTER With ANTHANTHRONE.

Evidence so far accummulated has shown that the condensations involving the use of acetone, acetophenone, and benzyl cyanide, have produced mixtures of products of varying complexity due to chain formation. A possible explanation to account for this phenomenon is that the attachment of an anthanthronyl residue to the activated methylene group may render this combination even more reactive in the presence of alkali than was the original methylene compound, provided, of course, that the latter compound possessed more than one replaceable hydrogen atom.

One obvious method to prevent the occurrence of chain formation is to employ a reactive compound possessing only one replaceable hydrogen atom. Condensations involving compounds of this type do not come within the scope of the patent under consideration, but it was decided to investigate the possibility of effecting the condensation of α-cyanopropionic ester with anthanthrone in the presence of powdered potassium hydroxide. Care had to be exercised in the purification of the α-cyanopropionic ester because the presence of any of the lower homologue, cyanoacetic ester, would again result in a mixture of products being obtained.

A mixture of 1·5 gms. anthanthrone, 100 gms. anhydrous pyridine, 8 gms. α-cyanopropionic ester, and 12 gms. powdered potassium hydroxide were heated under reflux in an atmosphere of nitrogen. On applying heat, the originally orange-red mixture assumed a purple colour and after heating for four hours, a green tint had appeared. The mixture was then cooled, made slightly acid, and filtered immediately. A dark-red solid separated from the brown filtrate. This solid, after washing and drying, weighed 1·05 gms. A trace of the solid dissolved to a green solution in concentrated sulphuric acid. A sample of the solid was also tested for the presence of nitrogen, with negative result.

Since the product contains no nitrogen, it either consists entirely of unchanged anthanthrone or else the cyanopropionic ester derivative formed has been affected.by heating with the strong alkaline agent. The product was next tested by boiling with aqueous sodium hydroxide solution. It was found to be partly soluble in this reagent to form a reddish-purple solution which, when filtered off from the insoluble portion, precipitated a red solid on acidification. The condensation reaction has therefore produced an acid product containing no nitrogen, which possibly conforms to one of the following structures:-



I II

Compound II, the anthanthrone dipropionic acid, is the more likely alternative, since compound I, containing dibasic acid groupings, would probably lose carbon dioxide to form the monobasic acid derivative. The ester grouping also would be unlikely to remain unchanged after a prolonged period of heating in the presence of a strong alkali.

To ensure that no esterified carboxylic groups remained unaffected, the whole of the solid was boiled for six hours with 2 N-methyl-alcoholic potassium hydroxide solution, acidified, and filtered. The solid residue was then extracted with successive portions of hot aqueous alkali until the alkaline solution was colourless. Acidification of the reddish-purple alkaline filtrate yielded about 0·05 gm. of a brown acid product. The residue, insoluble in hot aqueous alkali, amounted to 0·6 gm. and was a bright orange-red colour. This solid, after careful washing, was found to produce a clear-green solution

in concentrated sulphuric acid and to be almost completely soluble in hot chlorobenzene. A sample, crystallised from hot chlorobenzene, proved on analysis to be unchanged anthanthrone.

The very small alkali-soluble fraction was found to be fairly soluble in cold water but not in a weakly acid solution. In order to remove adsorbed halide, it was washed very thoroughly in the centrifuge with an extremely dilute solution of nitric acid until the washings produced no turbidity with silver nitrate solution. The solid was then separated and dried at 100°C. In spite of prolonged washing, the analysis figures obtained, C = 59·7, H = 5·51%, were rendered valueless owing to the presence of 10% of an incombustible residue. Very careful washing of the product had been carried out and it is difficult to believe that this large amount of residue was due to adsorbed salts. A more likely explanation is that the residue was composed of silica produced by the alkali used attacking the glassware.

This experiment did, however, show that α-cyano-propionic ester condensed to a small extent with anthanthrone in the presence of powdered potassium hydroxide, but that the intermediate nitrogeneous compound had not been isolated.

ATTEMPTED CONDENSATION Of FORMAMIDE With ANTHANTHRONE.

Although it was realised at the outset that formamide is an amide of a different type to acetamide, which may be condensed with benzanthrone in the presence of alkali, it was considered worth while examining what happens when formamide is used in this reaction, since if condensation did occur the product would necessarily be a simple derivative of anthanthrone.

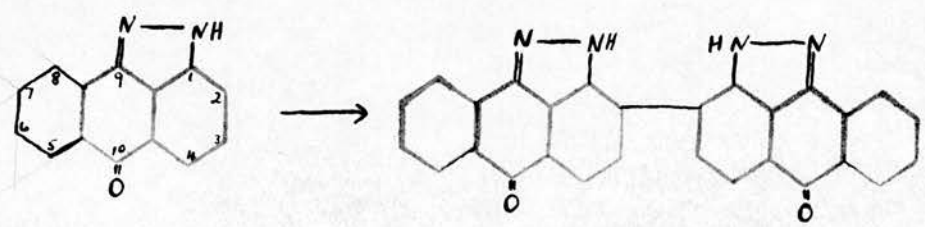
A condensation was therefore attempted by stirring a mixture of 1 gm. anthanthrone, 100 gms. anhydrous pyridine, 12 gms. powdered potassium hydroxide, and 20 gms. dry formamide, in an atmosphere of nitrogen. The mixture immediately warmed to about 35°C. and changed from orange-red to bright-red in colour. A great deal of ammonia was liberated from the formamide. The reaction was continued for 4 hours, the red mixture maintained at room temperature by external cooling. Ammonia was still being evolved at the end of this period, indicating the continued presence of unchanged formamide.

The reaction product was recovered in the usual way and 0·85 gm. of red material was obtained on filtration. The filtrate was almost completely colourless. The solid was tested for the presence of

nitrogen, and only a very small trace was detected. A portion was then boiled with aqueous sodium hydroxide, but no alkali-soluble product was present. On further boiling with alkali to hydrolyse any amide groupings which might have been present, no acid product was obtained. The alkaline solutions were perfectly colourless on filtration and it appeared that no reaction had taken place. The solid dissolved to a deep-green solution in concentrated sulphuric acid, indicating that the anthanthrone had been recovered unchanged. The small trace of nitrogen found to be present was probably due to a trace of adhering pyridine, and the reddish colour of the solid to a different aggregation of the anthanthrone particles.

ATTEMPTED CONDENSATION Of ACETONE With 1:9-Pyrazole-anthrone.

In the event of the condensation ofacetone with 1:9-pyrazole-anthrone proving successful, an investigation of the products promised to be less laborious than in the acetone-anthanthrone condensation,owing to the lower melting point and greater solubility of the parent compound. 1:9-Pyrazole-anthrone forms yellow-green needle crystals, m.p. 277-278°C., and is soluble to a much greater extent in organic solvents than anthanthrone. It dissolves to a red fluorescent solution in methyl alcoholic potassium hydroxide (used as a standard test for the presence of the condensation products) and to a yellow solution with weak green fluorescence in concentrated sulphuric acid. No information was available concerning the reactive positions in the presence of alkalis of the 1:9-pyrazole-anthrone molecule, except that on fusion with potassium hydroxide in ethyl alcohol, the 2-position is attacked with the formation of pyrazole-anthrone-yellow:-



Pyrazole-anthrone-yellow.

Substituted derivatives of 1:9-pyrazole -anthrone are therefore of potential value as dyestuffs.

The condensation of acetone with 1:9-pyrazole-anthrone was first attempted employing the milling process. 1 Gm. pyrazole-anthrone, 100 gms. acetone, 5 gms. powdered potassium hydroxide, and 100 gms. dry pyridine were mixed in a bottle with glass balls. The mixture immediately turned a red colour with orange fluorescence. On commencing agitation, the mixture warmed slightly but no colour change developed during 3 hours. The mixture was then diluted with 60 gms. alcohol and simultaneously cooled and acidified with dilute hydrochloric acid. The yellow acid mixture was then filtered and the yellow solid washed well with water and dried. Weight 1·0 gm., m.p. 274-278°C.

The product was then compared by mixed melting point with pure 1:9-pyrazole-anthrone. The mixture melted at 274-279°C., indicating that the starting material had been recovered unchanged. The colour reactions given by the product with methyl alcoholic potassium hydroxide solution and with concentrated sulphuric acid were identical with those of 1:9-pyrazole-anthrone. No reaction had apparently occurred under the above conditions and it was decided to apply a more vigorous treatment.

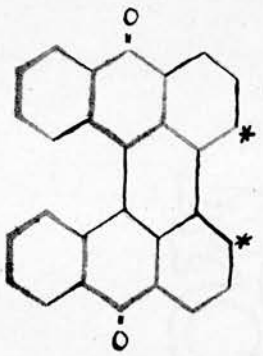
Attempted Condensation of Acetone with 1:9-pyrazole-anthrone at 50°C.

In this instance no pyridine was used, excess acetone playing the part of the solvent. A mixture of 1 gm. 1:9-pyrazole-anthrone, 12 gms. powdered potassium hydroxide, and 100 gms. acetone were stirred in a flask immersed in a water-bath at 50-55°C. An orange-red colouration quickly developed which gradually darkened, until after 3 hours the mixture was brown. The mixture was then diluted with 60 gms. alcohol, cooled and acidified, and allowed to stand overnight. On filtering the acid mixture, brown-yellow flakes separated which were washed with water and dried. Weight, 0·9 gm.

Traces of this solid dissolved to a red solution with orange fluorescence in methyl alcoholic potassium hydroxide, and to a yellow-brown solution with weak fluorescence in concentrated sulphuric acid. It melted at 277-280°C. with darkening at 260°C. These are substantially the properties of 1:9-pyrazole-anthrone , so a comparison by mixed melting point was made. The mixture gave m.p. 277-280°C. with darkening at 260°C. The starting material again had therefore been recovered unchanged, and under the conditions described, no appreciable reaction had occurred.

ATTEMPTED CONDENSATION of ACETONE With HELIANTHRONE.

Helianthrone is a cyclic ketone of the following constitution:-



No precise information about the reactivity of the helianthrone molecule in the presence of alkalis was available, but if condensation occurred, the two positions marked * might be expected to be reactive by analogy with benzanthrone, in which hydrogen in position 2 para to the ketonic group is attacked..

A condensation was carried out using the milling method. 2 Gms. helianthrone, 67 gms. acetone, 15 gms. powdered potassium hydroxide, and 137 gms. dry pyridine were mixed in a bottle with glass balls. The mixture immediately developed a brown colour and the colour did not change appreciably during 4 hours of agitation at room temperature. No perceptible temperature rise was noted. The mixture was simultaneously cooled and acidified and the dark-brown solid recovered by filtration. Traces of this product dissolved to a

greenish-blue solution in concentrated sulphuric acid and to a brown solution in methyl alcoholic potassium hydroxide. Pure helianthrone dissolves to a green solution in concentrated sulphuric acid. Samples of the condensation product and of helianthrone, dissolved in concentrated sulphuric acid, developed an orange-red colouration on standing overnight. This was probably due to sulphonation.

The condensation product was extracted with cold normal methyl alcoholic potassium hydroxide solution and the solution filtered immediately into dilute hydrochloric acid. The brown solid which appeared was washed five times with hot water in the centrifuge and dried. Weight 0·18 gm., corresponding to a 9% yield. The alkali soluble material was then boiled with 50 mls. monochloro-benzene and filtered hot. Four-fifths of the solid passed into solution. The filtrate was then precipitated with light petroleum, the brown solid centrifuged, washed well with petroleum, and dried. Analysis gave the values C = 79·71, H = 4·60%. A diacetonyl-helianthrone would require C = 82·59, H = 4·45%.

The experimental and calculated hydrogen values show a reasonable correspondence but the carbon values are not in agreement. Helianthrone requires C = 87·93 , H = 3·66%. Some reaction therefore seems to have occurred but purification of the condensation product

is a matter of extreme difficulty. Helianthrone is appreciably soluble in methyl alcohol. Unchanged helianthrone may therefore be present after extraction of the alkali soluble content by methyl alcoholic potassium hydroxide solution. The solubility of helianthrone in higher alcohols was examined and it was found to be, if anything, more soluble in these than in methyl alcohol. Therefore, using propyl alcoholic potassium hydroxide, for example, in the extraction of the alkali soluble material would offer no advantage. Time did not permit a thorough investigation into methods of isolating individual products from the condensation mixture, and it was evident that a new technique would have to be adopted.

CONDENSATION Of BENZYL CYANIDE With BENZANTHRONE.

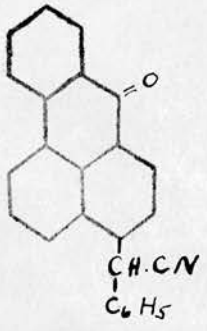
As has been stated in the Introduction, no information regarding the hydrolysis of benzylcyano-benzanthrone is contained in the patent. For this reason some of this compound was prepared and its hydrolysis with acid and alkaline reagents examined.

The condensation was carried out under the conditions described in B.P. No. 319,593. Benzyl-cyanide, 13·5 gms, was dropped into a stirred mixture of 9 gms. benzanthrone, 27 gms. powdered potassium hydroxide, and 45 gms. anhydrous pyridine and maintained at 10-15°C. in an atmosphere of nitrogen. The originally greyish-green mixture immediately turned olive-green and a very dense bluish-green colour gradually developed. The reaction mixture warmed up slightly at first and had to be cooled to the desired temperature. Stirring was continued for 3 hours, throughout which interval the dense green colour of the mixture persisted. The mixture was then diluted with 120 mls. ethyl alcohol and poured into a mixture of ice and dilute aqueous hydrochloric acid in an amount sufficient to acidify the mixture. The mixture was then a brown colour.

On filtration of the acid mixture, a dark resinous mass was separated from a brown filtrate. The solid

residue was washed on the filter with acetone and on drying, 6·5 gms. of a brown solid were obtained, m.p. about 200°C. This represents a yield of crude product amounting to 48% of the theoretical. Traces of this substance produced a deep-blue colour in methyl alcoholic potassium hydroxide solution and a deep orange-red solution with fluorescence.of the same colour with concentrated sulphuric acid. The main bulk of the solid was then boiled with benzene and filtered hot. 0·3 Gms. of a dark brown insoluble residue were left on the filter, which gave a dark violet-blue colour in methyl alcoholic potassium hydroxide solution. The clear orange filtrate deposited orange-yellow crystals on cooling. Weight 4·0 gms., m.p. 207-208°C. A sample of this compound dissolved to a pure blue solution in methyl alcoholic potassium hydroxide solution. Further purification of a sample for analysis yielded a product, m.p. 209-211°C., and gave the values C = 87·36, H = 4·12, N = 4·11%, corresponding with a benzylcyano-benzanthrone which requires C = 87·0, H = 4·35, N = 4·06%.

By analogy with the acetonyl derivative of benzanthrone this compound was assumed to be a 2-benzylcyano-benzanthrone of the following constitution:-



Concerning the hydrolysis of this compound no information was available. It was therefore decided to study the effect of heating the compound with an acid hydrolysing mixture. 1 Gm. of 2-benzylcyano-benzanthrone was boiled under reflux with 75 mls. of an acid hydrolysing mixture of glacial acetic acid, concentrated sulphuric acid, and water in the proportions 4:2:1 respectively. On warming, practically all the solid dissolved in a few minutes to an orange-coloured fluorescent solution. On boiling for a short time, the colour became dark red. Refluxing was continued for $6\frac{3}{4}$ hours. The solid was recovered by pouring the acid mixture into water and filtering. The product (0·9 gms.) produced no colour with methyl alcoholic potassium hydroxide solution and chemical change had therefore occurred. It melted at 179-181°C., with softening at 178°C., and traces were found to be soluble in aqueous sodium hydroxide. On crystallisation from hot benzene, 0·5 gms. of long, flat, micro-needles separated, m.p. 173-181°C. (Fraction A). This product was tested and contained no nitrogen. The benzene mother-liquor taken to dryness yielded 0·4 gms. of brownish-yellow solid, m.p. 178-181°C., with softening at 174°C. (Fraction B).

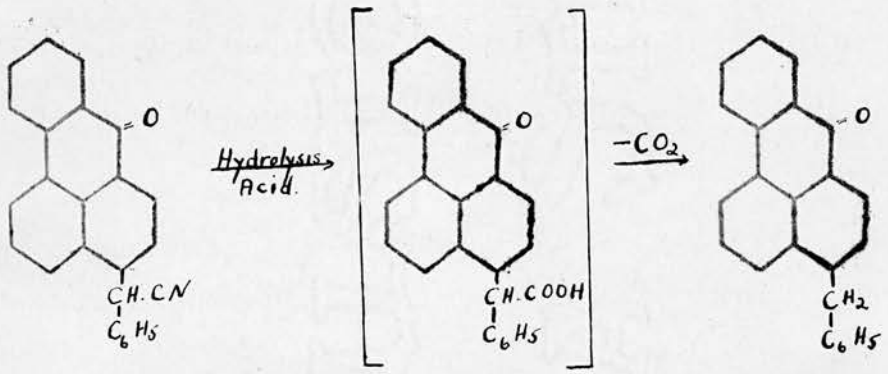
The solid of fraction A on boiling with dilute aqueous sodium hydroxide gave a yellow (green fluorescent)

solution which on filtration and acidification produced only a minute trace of solid. The recovered material, insoluble in hot alkali, now gave m.p. 178-181°C. with softening at 175°C. Under the microscope the crystals appeared to be pitted. The whole sample was dissolved in the minimum amount of hot pyridine and diluted with aqueous sodium hydroxide followed by water. On filtering, the filtrate was still coloured, showing that simple boiling with aqueous sodium hydroxide is insufficient to remove all the acid product. The recovered solid gave m.p. 176-180°C. Recrystallisation from glacial acetic acid yielded a product, m.p. 180-181°C.

The solid of fraction B was then treated similarly with hot pyridine and dilute aqueous sodium hydroxide. The recovered solid now gave m.p. 178·5-180°C. Recrystallisation from glacial acetic acid yielded a product, m.p. 181-182°C. The alkaline extracts from fractions A and B yielded only a fraction of a milligram of precipitated acid on adding hydrochloric acid, although all colour was thereby discharged from the liquid.

The products obtained from A and B were united and weighed 0·5 gms. The whole was then repeatedly crystallised from glacial acetic acid to give pale-yellow needle crystals, m.p. 182-182·5°C., a trace of which dissolved to an orange-red solution with golden

fluorescence in concentrated sulphuric acid. Analysis of a sample of this product yielded the following values: C = 89·3%, H = 5·2%. A benzyl-benzanthrone would require C = 90·0%, H = 5·0% and the experimental values obtained thus correspond closely with the calculated values. It is concluded therefore that acid treatment has produced 2-benzyl-benzanthrone according to the following reactions:-



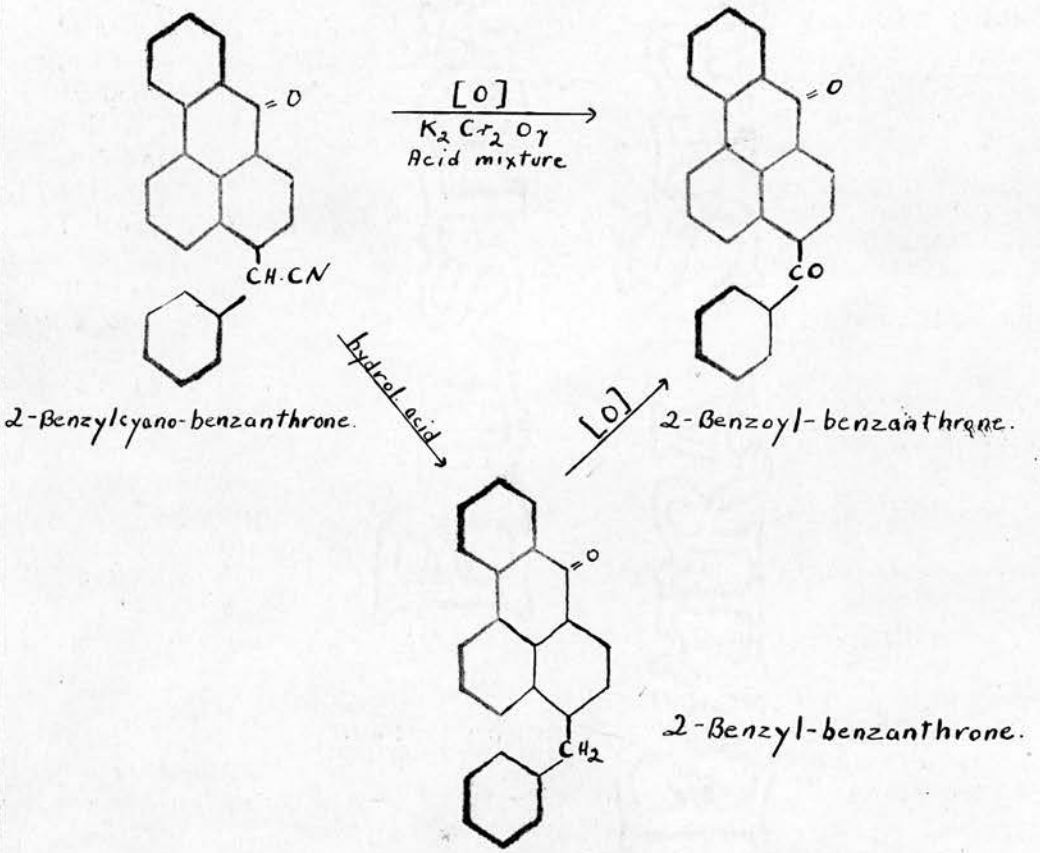
2-Benzylcyano-benzanthrone. Intermediate unstable acid. 2-Benzyl-benzanthrone.

An unstable intermediate carboxylic acid derivative is apparently formed which, by loss of carbon dioxide, immediately forms 2-benzyl-benzanthrone. This would account for the trace of acid product isolated above, which was insufficient for analysis.

Attempted oxidation of 2-benzylcyano-benzanthrone to 2-benzoyl-benzanthrone.

2-Benzylcyano-benzanthrone has been shown (page 89) to hydrolyse to 2-benzyl-benzanthrone on being heated with an acid hydrolysing mixture of glacial acetic acid, concentrated sulphuric acid, and water, in the

proportions 4:2:1 respectively. As is shown later, hydrolysis with methyl alcoholic potassium hydroxide solution in presence of air yields 2-benzoyl-benzanthrone. For this reason hydrolysis and oxidation of 2-benzyl-cyano-benzanthrone was attempted in one operation by the use of the above acid mixture with the addition of powdered potassium dichromate:-



0·3 gms. 2-Benzylcyano-benzanthrone (purified).

0·17 gms. Potassium dichromate (powdered).

16 mls. Glacial acetic acid.

8 mls. Concentrated sulphuric acid.

4 mls. Water.

The above mixture was heated under reflux and at the beginning had a warm brown colour. This colour became darker as heating was continued. After 7 hours, half of the acid mixture was precipitated in water and filtered. A trace of the solid produced no colour with methyl alcoholic potassium hydroxide solution. Some chemical change had then occurred. The whole of the mixture was therefore poured into water and the dark brown solid recovered by filtration. Purification of this solid from benzene, using animal charcoal, and subsequent recrystallisation with glacial acetic acid, produced brownish-yellow crystals of m.p. 178-181°C. This product was compared by mixed melting point with the 2-benzyl-benzanthrone prepared previously (page 88). No depression was noted and it was evident that although the 2-benzylcyano-benzanthrone had been hydrolysed by the acid mixture, the potassium dichromate had not effected oxidation.

Oxidation of 2-Benzylcyano-benzanthrone with Sodium Dichromate in Glacial Acetic Acid.

1·5 gms. 2-Benzylcyano-benzanthrone.

4·5 gms. Sodium dichromate (powdered)

100 mls. Glacial acetic acid.

The above mixture was heated under reflux and soon developed a brownish tint. After 20 minutes the

colour of the mixture was green. After heating for 2½ hours the mixture was poured into water, and a yellowish-brown solid appeared in a deep green solution. The solid was coagulated by heating, filtered, washed, and dried, when 1·2 gms. of a brownish-yellow resinous material were obtained. Recrystallisation from glacial acetic acid yielded 1 gm. of a brownish-yellow product melting mainly at 167-172°C., although a trace did not melt until 225°C. Purification by means of an aluminium oxide adsorption tube was then resorted to.

The solid was dissolved in benzene, and light petroleum, b.p. 60-80°C., added to the cold solution in such an amount that the solid was just retained in solution. The solvent mixture then consisted of 55 parts of benzene and 45 parts of light petroleum. The aluminium oxide adsorption tube was prepared, using the same mixture of solvents. On introducing the solution of the compound under investigation into the tube, a bright yellow band, 1" in length, spread down the tube, followed by an orange band, ¼" in length. A small brown band remained at the top of the tube. The proportion of benzene was increased during the washing process, when the yellow band was washed through the tube and the solution collected. On evaporation of the solvent, about 0·3 gms. of a yellow solid were obtained, m.p. 175-177°C.

A sample of this compound produced no colour in methyl alcoholic potassium hydroxide solution and no longer contained nitrogen. Comparison by mixed melting point with the 2-benzyl-benzanthrone prepared previously produced a depression of the order of 30°C. and indicated that some other benzanthrone derivative had been isolated. Further purification of the product obtained above from glacial acetic acid produced an analytical sample of m.p. 179-180°C. Analysis of this gave C = 86·64, H = 4·4%. These values correspond closely with those required for a benzoyl-benzanthrone, for which C = 86·2 and H = 4·2%, and it is concluded that the product is 2-benzoyl-benzanthrone. A compound of this structure was described in 1932 by Kacer (D.R.P. 557,249), who obtained it from 2-benzyl-benzanthrone by oxidation with H_2SeO_3 and water under pressure, which was stated to result in the formation of a very pure 2-benzoyl-benzanthrone, m.p. 174-176°C. The source of the benzyl derivative is not given.

HYDROLYSIS OF 2-BENZYLCYANO-BENZANTHRONE WITH METHYL ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION.

Attention was next turned to the reaction between 2-benzylcyano-benzanthrone and methyl alcoholic potassium hydroxide solution. 0·5 Gms. of purified 2-benzylcyano-benzanthrone were heated under reflux with 60 mls. of 2N methyl alcoholic potassium hydroxide solution. An intense blue solution resulted on first mixing the reagents. No further colour change developed during 8 hours heating, but on allowing the flask to stand open to air over-night, yellow crystals separated and the solution turned a brown colour with exceptionally strong green fluorescence. The mixture was then diluted with water, filtered, the yellow needle-shaped crystals washed well with water, and dried. The product weighed 0·5 gms. and melted at 175-177°C. Purification of the product from benzene, using animal charcoal, gave bright-yellow crystals of m.p. 176-177°C.

This product was tested for nitrogen but gave a negative result. Comparison by mixed melting point of a sample of this product with 2-benzyl-benzanthrone showed by the resulting depressed melting point that the compounds were not identical. Further purification of the product for analytical purposes raised the

melting point to 178-180°C. The analytical values obtained were: C = 86·1, H = 4·5%.

This compound was next compared by mixed melting point with the 2-benzoyl-benzanthrone whose preparation was described on page 91. No depression was noted, indicating an identical constitution for both products. Benzoyl-benzanthrone requires the analytical values C = 86·2, H = 4·2%, which agree closely with those obtained for the above product. It was therefore concluded that 2-benzoyl-benzanthrone has been produced.

This reaction is a very unusual one, but an explanation can be put forward for the fact that the conversion of 2-benzylcyano-benzanthrone to 2-benzoyl-benzanthrone was completed only on allowing the reagent vessel to stand open to air. The reaction is obviously an oxidation and the presence of air or other oxidising agent is essential. The next step was to carry out the process with a liberal supply of air or of pure oxygen.

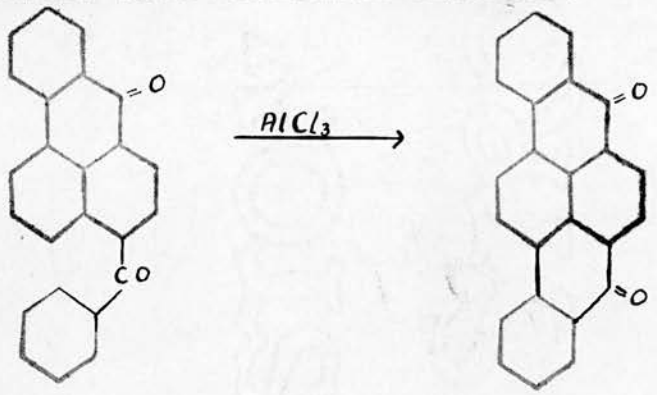
Two separate portions of the 2-benzylcyano-benzanthrone were therefore heated under reflux with a current of air passing through one flask and a current of oxygen passing through the other. In neither case was the original blue colour discharged during 10 hours heating, but on standing overnight the reaction completed itself. In each case an approximately quantitative yield of comparatively pure 2-benzoyl-

benzanthrone was obtained.

A similar process was attempted by heating 2-benzylcyano-benzanthrone with a 50% aqueous-alcoholic solution of potassium hydroxide in a current of air. After heating for 2 hours the mixture turned a dark green. Tests made on a sample of the recovered solid showed, however, that the product still produced a blue colour with methyl alcoholic potassium hydroxide solution and that conversion was not complete. Further heating produced the same result. A solution of potassium hydroxide in methyl alcohol containing 25% of water was then employed and a similar green colour soon developed. Tests made, however, showed that unchanged 2-benzyl-cyano-benzanthrone was still present, even after 10½ hours heating. The colour change occurring during the process probably indicates that 2-benzoyl-benzanthrone is being formed to a certain extent on the surface of the 2-benzylcyano-benzanthrone, but that due to the insolubility of the latter compound in the aqueous alcoholic mixture, no further conversion can be effected.

The treatment of 2-benzylcyano-benzanthrone by boiling with methyl alcoholic potassium hydroxide solution in the presence of air therefore appears to offer a practicable method for the preparation of the technically valuable 2-benzoyl-benzanthrone in excellent yield. By direct oxidation of the former compound

with sodium dichromate in glacial acetic acid, a certain amount of resinification occurs and the yield is poor. 2-Benzoyl-benzanthrone is an important intermediate for the preparation of the following symmetrical cyclic ketone which may be prepared by treating 2-benzoyl-benzanthrone with aluminium chloride:



Substituted derivatives of this latter compound are potentially valuable as dyestuffs.

An attempt to prepare benzyl-benzanthronyl carbinol by less vigorous oxidation of 2-benzylcyano-benzanthrone proved unsuccessful. A mixture of 1 gm. 2-benzylcyano-benzanthrone, 1 gm. powdered sodium dichromate, and 65 mls. of glacial acetic acid changed on heating from the original orange colour to a green in 10 minutes. Recovery of the product and purification by the chromatographic method showed, however, that 2-benzoyl-benzanthrone was produced in poor yield by this milder treatment.

PREPARATION Of The STARTING MATERIALS.

Powdered Potassium Hydroxide.

The potassium hydroxide was supplied in crushed form by Messrs Hopkin and Williams. It was sieved through a No. 40 mesh and stored in a desiccator.

Anthanthrone.

15 Gms. Dimethyl ester of 1:1'-dinaphthyl-8:8'-dicarboxylic acid (purified).

150 Gms. Concentrated sulphuric acid.

The mixture was heated at 100°C. for 1 hour with occasional stirring. A red colour developed which denoted the formation of an intermediate half-cyclised product, but this was soon replaced by a deep-green solution on completion of the reaction. The cooled green solution was then poured into ice-cold water, the red flocculent precipitate of anthanthrone filtered off, washed with water, and dried.

Yield, 14·5 gms. (quantitative);

M.p. $>$ 360°C.

1:9-Pyrazole-anthrone.

The preparation was first attempted from 1-amino-anthraquinone, as described in Berichte, 45, II, 2233 et seq., and involved the isolation of anthraquinonyl-1-hydrazine. This method was not successful, however,

due to decomposition of the products. Decomposition also occurred in an attempt to prepare anthraquinonyl-1-hydrazine from 1-chloro-anthraquinone (Ber., 45, II, 2245 and 2239). The preparation of 1:9-pyrazole-anthrone was then attempted as follows (E.P. 297366):-

A thick aqueous paste of 10 gms. 1-chloro-anthraquinone, 10 gms. hydrazine sulphate, and 30 gms. calcium hydroxide was heated for 6 hours in an autoclave at 200°C. By this process a black mass was obtained from which a small quantity of impure 1:9-pyrazole-anthrone was extracted by means of concentrated hydrochloric acid. Subsequent purification from o-dichlorobenzene yielded a product, m.p. 270-278°C.

The following successful preparation was then carried out, as advised by I.C.I. Dyestuffs Group:-

Diazotisation.

Crushed sodium nitrite, 14·4 gms., was fed during 30-40 minutes below 25°C. into 160 gms. of 93% sulphuric acid. To ensure complete solution, the temperature was raised to 85-90°C. and held there for 1½ hours. When the nitrite was completely dissolved, 40 gms. of 1-aminoanthraquinone were added during 20-40 minutes at 50-60°C. The melt was stirred at 60°C. for 1 hour or longer until all lumps of 1-amino-anthraquinone were dissolved, and then tested for completeness of diazotisation. This was done by diluting 3 drops of the melt in a small quantity of

water. The diazotisation was complete when a white to yellowish precipitate formed with no reddish-brown colour of unchanged amine.

When the diazotisation was complete, the melt was drowned in 240 gms. water and 240 gms. ice and the volume adjusted to 720 mls. The suspension was filtered off at 0-5°C. and washed with not more than 20 gms. of cold water. The cake was mixed with ice and water to give a total volume of 360 mls. at 0-10°C.

Reduction.

While the diazotisation was being carried out, 160 gms. of sodium sulphite crystals and 104 gms. of soda ash were dissolved in water to give a total volume of 800 mls. at 15-20°C. Into this solution the diazo mixture was slowly run with good agitation. After stirring for 1 hour, the charge was heated to 100°C. during the course of 1 hour, maintained at this temperature for 2 hours, after which heating was discontinued.

Hydrolysis.

The solution was carefully acidified with about 168 gms. of 30% hydrochloric acid and then treated with an additional 80 gms. of the same acid. Sulphur dioxide was given off during the addition of the acid and a suction was therefore kept on the vessel to carry away fumes. The hydrolysis was completed by

heating again at 100°C. for 1 hour, when a spot test on filter paper showed a pale-yellow ring instead of the original red ring. The anthraquinone-1-hydrazine was filtered off cold, washed acid-free, and dried at 70-90°C.

1:9-Pyrazole-anthrone.

10 Gms. anthraquinone-1-hydrazine

30 Gms. 97% sulphuric acid

The anthraquinone-1-hydrazine was dissolved at 10-30°C. in the sulphuric acid and the whole heated at 110°C. for 1 hour. The resultant pyrazole-anthrone was then precipitated by the addition of 26 gms. of water at 50-60°C. and filtered off at 30°C. It was washed with 32 gms. of cold 52% sulphuric acid, and then boiled with 100 mls. of water, filtered cold, washed acid-free, and dried at 100°C.

The yield of the hydrazine was 23 gms. (a quantity which precipitated in the acid filtrate was not recovered, as sufficient had been obtained for immediate requirements). 16 Gms. of pyrazole-anthrone were obtained which were crystallised from benzene, using animal charcoal. Yield, 11 gms.; m.p., 275-278°C.

Helianthrone.

Communicated by I.C.I. Dyestuffs Group.

1:1'-Dianthraquinonyl.

9·6 Gms. 1-chloroanthraquinone were warmed with

24 mls. nitrobenzene and heated to boiling to remove traces of moisture, 5·2 gms. natural copper were added, and the whole heated to boiling under reflux. After a short time the dianthraquinonyl formed began to separate in small yellow prisms, and after 3 hours the mass was diluted with benzene, filtered, and the residue treated with dilute nitric acid (to remove copper). The product thus obtained (6·24 gms., i.e., 75% of theory) was in the pure state.

Helianthrone.

Scholl and Mansfield, Ber., 1910, 43, 1734; also G.P. 190799, Frdl., 9, 801.

5 Gms. 1:1'-dianthraquinonyl were dissolved in 150 gms. 96% sulphuric acid, and 5 gms. of copper powder added. The yellow-brown solution changed on addition of the copper to a dark green. The mixture was stirred for 15-20 minutes at 40-50°C., filtered to remove excess copper, and the dyestuff precipitated by pouring into ice and water. The solid was filtered off, washed with water, and dried at 150°C.

The product was a yellow-brown powder, insoluble in water, aqueous alkalis, or acids, but easily soluble in concentrated sulphuric acid to a green solution. It was difficultly soluble in high-boiling solvents. Recrystallised from xylene or nitrobenzene, it formed yellow-brown crystals.

α-Cyanopropionic ester.

The preparation was first attempted from cyano-acetic ester as described by Hessler (J.A.C.S., 35, 991). This process involved an elaborate purification and gave a very small yield of pure α-cyanopropionic ester. The usual method employed for the preparation of cyanoacetic ester from mono-chloracetic acid was therefore adapted, as follows, for the preparation of α-cyanopropionic ester from α-chloro-propionic acid.

50 Gms. α-chloropropionic acid (in 25 mls. water)

85 Gms. Sodium carbonate (hydrated)

39 Gms. Sodium cyanide (in 70 mls. water)

The powdered sodium carbonate was added to the solution of α-chloropropionic acid. As the reaction was exothermic the vessel was kept in water at room temperature. The alkaline solution was then poured into a hot solution of 39 gms. sodium cyanide in 70 mls. water, and the mixture boiled for 5 minutes to complete the reaction. The solution was cooled below 20°C., stirred, and concentrated sulphuric acid added, drop by drop, keeping the temperature below 25°C., until it was just acid to logwood paper. Considerable frothing occurred at this stage. The sodium chloride which now separated was removed by filtration, transferred to a flask and shaken with 83 mls. of absolute alcohol.

It was filtered and the residue washed with a further 28 mls. of alcohol. The alcoholic extract was preserved for further treatment.

The filtrate from the salt was evaporated in vacuo on the water-bath at 70-80°C., the residue well shaken with the above alcoholic extract, and filtered. The solid was again treated with 56 mls. of absolute alcohol and filtered. The combined alcoholic extracts (about 170 mls.) were distilled in vacuo on a water-bath at 50-60°C., which removed the greater portion of the solvent. The residue was mixed with 39 mls. absolute alcohol and 2 mls. concentrated sulphuric acid and heated in a paraffin bath at 100-110°C., while the vapour from 170-220 mls. of alcohol was introduced. It was then heated for a further half-hour and cooled. Ice was now added, and the cooled product extracted with ether. The ether extract was washed with sodium carbonate solution and dehydrated over calcium chloride.

The solvent was distilled from a water-bath and the residual α-cyanopropionic ester purified by distillation in vacuo in an all-glass apparatus. Yield, 21 gms. (36%); b.p., 83-84°C./12 mms.

Drying of Formamide.

The formamide was supplied by The British Drug Houses Ltd. and was purified by careful fractional distillation under diminished pressure, using a fine capillary air inlet. B.p.,103·5-104°C./10mms., using an all-glass apparatus.

S U M M A R Y.

That the condensation of acetone with anthanthrone in the presence of powdered potassium hydroxide undoubtedly occurs to some extent is evident from the fact that the product of the reaction forms coloured salts with solutions of potassium hydroxide in alcohol or acetone. The condensation is not, however, of the same simple nature as that undergone by benzanthrone. The product consists of a complex mixture, the component fractions of which differ greatly in solubility in ordinary organic solvents. The formation of a multiplicity of products can only be explained on the assumption that chain reactions are taking place. The condensation is evidently not a simple one in which only one of the reactive hydrogen atoms in the acetone molecule is substituted. Diacetonyl-anthanthrone may be formed as an intermediate product but it is certain that the remaining activated hydrogen atoms in the acetonyl side-chains are free to react with more anthanthrone. This process may apparently go on indefinitely, and satisfactorily explains the diversity of products obtained in the condensation. The use of a milder alkaline condensing agent failed to reduce the complexity of the product and carrying out the

condensation with all the reagents in the liquid phase was also unsuccessful.

The condensation of anthanthrone with acetophenone and with benzyl cyanide yielded similar results. In each case, colour manifestations indicated that a reaction was going forward but the same multiplicity of products was recovered. When benzyl cyanide was condensed with anthanthrone at 100°C. the product appeared to be less complex, probably because the derivative initially formed on the surface of the potassium hydroxide particles rapidly underwent further change at the high temperature and in contact with the alkali, in such a manner that it was no longer readily attacked by more benzyl cyanide. No homogeneous product could, however, be isolated from the mixture. Use of the chromatographic method for the separation of any of the mixtures obtained from these condensations met with no success.

Attempts to condense anthanthrone with a reactive methylene compound having only one hydrogen atom available for substitution failed to yield a product whose constitution could be confirmed. α-Cyanopropionic ester condensed to a small extent with anthanthrone but formamide did not react.

The condensation of anthanthrone with acetone, acetophenone, and benzyl cyanide yielded products whose behaviour on hydrolysis was quite different from

the corresponding benzanthrone derivatives. A derivative, which from analytical results was at first thought to be a diacetonyl-anthanthrone, was extremely resistant to acid and alkaline hydrolytic agents and required fusion with alkali for hydrolysis. No individual compound could, however, be isolated from the resultant mixture, which again illustrates the complex nature of the condensation product. The main product of the condensation of anthanthrone with benzyl cyanide was extremely resistant to acid hydrolysis, but an alkali soluble fraction could be isolated which wasrapidly attacked by methyl alcoholic potassium hydroxide solution. This reaction appeared to correspond to the conversion of a benzylcyano to an amide derivative, although analytical confirmation of this could not be obtained. The condensation of anthanthrone with acetophenone yielded a product which was rapidly attacked by alcoholic alkali but which gave no simple hydrolysis product, again indicating that the reaction is of a complex nature.

No precise information could be obtained concerning the influence of temperature, presence or absence of air, time of contact of the reagents, or of the quantities of the reagents used, on the course of the reaction. Carrying out the condensation of anthanthrone with benzyl cyanide at 100°C. appeared to reduce the complexity of the product but, in general, raising the

temperature caused a more vigorous interaction of the reagents with the production of a proportionately greater diversity of products and also a greater amount of resinification. On the other hand, carrying out the condensation in the absence of air, for example, in a nitrogen atmosphere, appeared to reduce resinification. Increase in time of contact and in the quantities of the reagents both had much the same effect as raising the temperature. An increase in the time of contact of the reagents or in the proportions of the reagents with respect to the compound being condensed led to a more vigorous reaction and diversity of products, and more especially to products of greater complexity as indicated by decreasing solubility in organic solvents.

The condensation of acetone with 1:9-pyrazoleanthrone and with helianthrone was attempted. No condensation occurred between acetone and 1:9-pyrazoleanthrone in the presence of powdered potassium hydroxide, either in the cold or at the temperature of boiling acetone. In the case of the condensation of acetone with helianthrone, a slight colour change appeared to indicate that some reaction occurred, but difficulties were encountered when a separation of the products was attempted. The usual method of extraction with alcoholic potassium hydroxide solution could not be employed because helianthrone is moderately soluble in

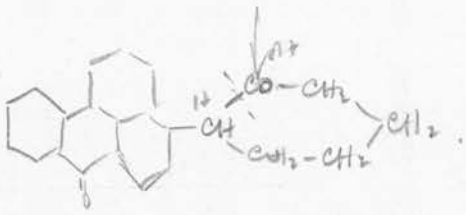
cold alcohol. It is possible that in this condensation also chain reactions are going forward.

A study of the reactions undergone by 2-benzylcyano-benzanthrone produced some interesting results. Hydrolysis with an acid mixture yielded 2-benzyl-benzanthrone in moderate yield. A carboxylic acid was presumably formed as an intermediate which lost carbon dioxide to form the benzyl compound. 2-Benzoyl-cyano-benzanthrone was oxidised directly to 2-benzyl-benzanthrone by means of a mixture of sodium dichromate and glacial acetic acid, but a very impure product was obtained in poor yield. Treatment of 2-benzylcyano-benzanthrone with methyl alcoholic potassium hydroxide solution with access of air resulted in an oxidation going forward yielding pure 2-benzoyl-benzanthrone in good yield. This was an unexpected and important result because of the excellent yield and quality of the product. Carrying out the reaction in an atmosphere of oxygen did not influence the course of the oxidation appreciably, and the use of aqueous-alcoholic potassium hydroxide solution showed that the presence of water was undesirable.

An attempt to form benzyl-benzanthrone-carbinol by mild oxidation of 2-benzylcyano-benzanthrone met with no success, impure 2-benzoyl-benzanthrone being recovered instead.

P O S T S C R I P T.

The author wishes to express his indebtedness to Dr Rule for his helpful advice and assistance during the course of this work, and to Imperial Chemical Industries Limited (Dyestuffs Group) for a grant and chemicals.



$-CH_2(CH_2)_4.COOH$.

$-CH_2.CO\,CH_3$